Plant Nano Biology 1 (2022) 100008

Contents lists available at ScienceDirect

Plant Nano Biology

journal homepage: www.journals.elsevier.com/plant-nano-biology

Nano-enabled weed management in agriculture: From strategic design to enhanced herbicidal activity

Mariana M.L. Forini[a,1], Montcharles S. Pontes[b,1], Débora R. Antunes[a], Pedro H.C. de Lima[a], Jaqueline S. Santos[c], Etenaldo F. Santiago[b], Renato Grillo[a,*]

[a] São Paulo State University (UNESP), Department of Physics and Chemistry, Faculty of Engineering, Ilha Solteira, SP, Brazil
[b] Plant Resources Study Group, Natural Resources Program, Center for Natural Resources Study (CERNA), Mato Grosso do Sul State University (UEMS), Dourados, MS, Brazil
[c] Genetics Department, Luiz de Queiroz College of Agriculture (ESALQ), University of São Paulo (USP), Piracicaba, SP, Brazil

ARTICLE INFO

Keywords:
Agriculture
Nanopesticides
Weed control
Sustainable agriculture
Pest management

ABSTRACT

The use of nanotechnology has emerged in the agricultural sector. In recent years, several nano-enabled materials have been reported for weed control. Nano-enabled herbicides (also called nanoherbicides) can be designed from organic, inorganic, or hybrid materials. These materials have unique properties such as small size, specific surface area, and the ability to control the release of metal ions and organic molecules in the agricultural field. Some studies have reported the ability of nanoherbicides to provide better weed management compared to non-nanoformulations. However, studies regarding the environmental risk assessment and mechanisms of action of nanoherbicides in plants are still incipient. Nevertheless, they are essential to ensure a safe application for human health and the environment. In this review, we outlined the current understanding of nano-enabled herbicides as well as some strategic design to fabricate nanostructures for weed control. Also, a critical discussion regarding the fate, behavior and effects of nanoherbicides in plants was addressed in order to achieve products for environmentally friendly and sustainable agriculture.

1. Introduction

The world's population is expected to reach over 9.7 billion in 2050 (FAO, 2018). Moreover, with climate change impacts, soil erosion, and pre-harvest losses, the pressure to develop sustainable agriculture practices will further increase in the future (Popp et al., 2013; FAO, 2017; Wu and Li, 2022; Kah et al., 2019). Besides, agrochemicals are constantly used to improve food production. Their indiscriminate and abusive use causes damage to public health and environmental contamination (Dong et al., 2021a; Okeke et al., 2021). In the current scenario, approximately 4 million tones of pesticides are used annually for food production worldwide (Sharma et al., 2019; Wang et al., 2022a), of which 40% are herbicides, 30% are insecticides, and 20% are fungicides (Rojas et al., 2022). Nevertheless, the enormous quantity of pesticides used is linked to the low adhesion of these active ingredients (a.i.) on leaves, high soil sorption, and physicochemical instability (Dong et al., 2021b). Previous research has shown that less than 10% of conventional pesticides are targeted toward the plant (Zhao et al., 2018), and only 0.1% of these stay long enough to reach the targeted pest, while the rest goes directly to the surrounding environment (Liang et al., 2018; Mujtaba et al., 2020; Sarkar et al., 2022).

Nowadays, nanotechnology represents a novel direction for sustainable agriculture development (White and Gardea-Torresdey, 2018; Fraceto et al., 2016; Grillo et al., 2016; Wang et al., 2022a; Hofmann et al., 2020; An et al., 2022). One aspect of this expansion is the creation of nano-enabled materials for the controlled release of fertilizers and pesticides, as shown in Fig. 1. Moreover, nanopesticides were named as one of ten chemical innovations that will change the world in a sustainable way by the International Union of Pure and Applied Chemistry (IUPAC) (Gomollón-Bel, 2019). However, several countries do not have specific legislation for the use and commercialization of these products (Grillo et al., 2021a). In contrast, the USA registered its first nanopesticide in 2011, while China has already registered many others (Bocca et al., 2020). In the last decade, research has demonstrated the advantages of nanopesticides. However, environmental risk assessment studies in the field are still incipient, and they are critical to ensure safe application for humans and the environment avoiding alarmism or exaggerated expectations regarding results (Bocca et al., 2020; Santiago et al., 2020; Singh et al., 2020; Dong et al., 2021b; Grillo et al., 2021a).

* Correspondence to: Department of Physics and Chemistry, São Paulo State University (UNESP), Avenida Brasil, 56, Ilha Solteira, SP, Brazil.
E-mail address: renato.grillo@unesp.br (R Grillo).

[1] *These authors contributed equally to this work.*

https://doi.org/10.1016/j.plana.2022.100008
Received 16 June 2022; Received in revised form 26 June 2022; Accepted 27 June 2022

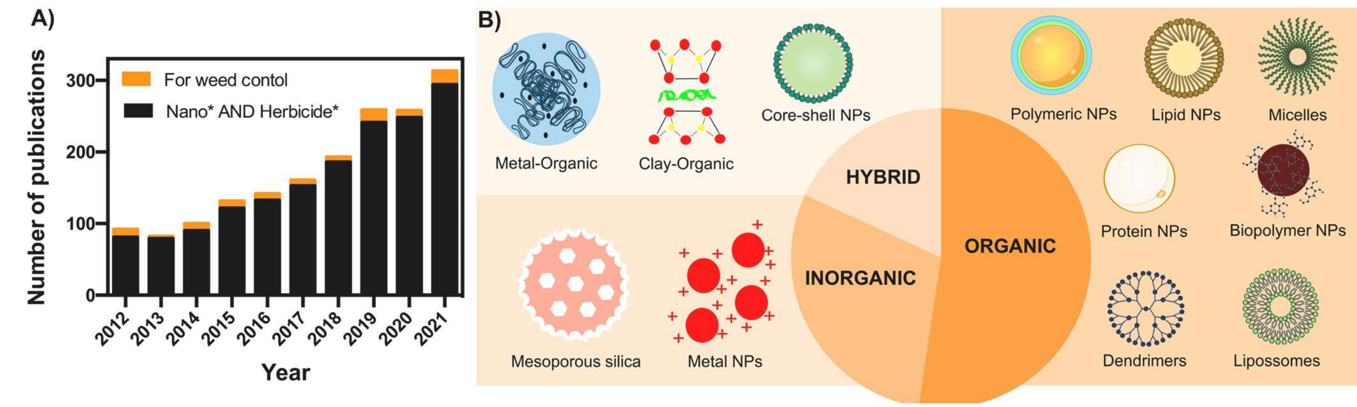

Fig. 1. **A)** Number of papers published annually using descriptors "nano* " and "herbicide* " in the ISI Web of Knowledge database from 2012 to 2021 **-** Orange bars show nano-enabled materials for weed control. **B)** Percentage distribution and some types of nanoherbicides developed in recent years.

Among the various nanopesticides, there are systems developed to control insects (Awad et al., 2021), weeds (Taban et al., 2020), bacterias (Tan et al., 2020), fungus (Machado et al., 2022), etc. Also, they can be categorized into three principal types: i) inorganic substances derived from metals, metals oxide, clay minerals, etc; ii) those in which the active ingredient (a.i.) is encapsulated in an organic nanocarrier derived from protein, polymers, lipids, and so on; or iii) hybrid nanostructures containing both inorganic and organic materials (Forini et al., 2020; Reddy and Chhabra., 2022). Furthermore, the evolution of nanoscience has brought strategies to architect more specific and intelligent nanopesticides (Abdollahdokht et al., 2022), and several examples have been reported in recent reviews (Rastogi et al., 2017; Grillo et al., 2021a; Kumar et al., 2021).

Recently, nano-enabled weed-controlling substances, commonly referred to as nanoherbicides, have demonstrated a potential use in sustainable agriculture. For example, a search in the Web of Science database (WoS) from 2012 to 2021 using the descriptors "nano* and herbicide* " yielded 1627 published scientific articles (Fig. 1**-A**). However, only ca. 100 peer-reviewed scientific articles were described as potential sources for weed control. According to this, organic nanoherbicides are the most studied, followed by inorganic and hybrid materials (Fig. 1**-B**), which can present different morphology and physicochemical properties. However, since the term "nano" is not always utilized in all scientific papers and some formulations may have a size higher than 100 nm (Chen and Wang, 2019; Takeshita et al., 2021), it is important to take these findings into account as a part of the research that has been developed in this sector. As a result, all nanoformulations found for weed control with the descriptors mentioned, whether or not associated with a.i., were designated nanoherbicides for the purposes of this review. Thus, we utline the current understanding of nano-enabled herbicides as well as some strategic design to fabricate nanostructures for weed control. A critical discussion addressing the fate, behavior, and impacts of nanoherbicides on plants was also addressed in order to develop solutions for ecologically friendly and sustainable agriculture.

2. Types of nano-enabled herbicides

Several studies were carried out for the development of nano-enabled herbicides due to their greater efficiency and environmental advantages (Xiang et al., 2017; Pontes et al., 2021; Oliveira et al., 2015a; Sousa et al., 2018). Nanoherbicides have shown better spread, adhesion, and longer contact time on the leaves and are able to control the release of a.i. (e.g., ions or biomolecules) (Grillo et al., 2021b; Peixoto et al., 2021). The effect of nanoherbicides on plants, however, is determined by their physicochemical properties, which include size, morphology, surface chemistry, concentration, etc. Therefore, the idea of strategic design has been applied in order to ensure the "optimal" properties of the nanoherbicides on target organisms. Several nanoherbicide examples can be found in the literature, and some of them are addressed in the sections that follow.

2.1. Organic nano-enabled herbicides

Organic nanomaterials are outstanding materials for assembling nanoherbicides, and they can be based on polymers (Chen and Wang, 2019; Takeshita et al., 2021), lipids (de Oliveira et al., 2015), lignocellulosic materials (Kumar et al., 2014; Lima et al., 2021), proteins (Heydari et al., 2021a), complex macromolecules as dendrimers (Petit et al., 2012; Maes et al., 2021), etc. Overall, several techniques can be reported to produce nanoherbicides, with the nanoemulsion method being one of the most utilized (Lim et al., 2012; Lim et al., 2013b; Guo et al., 2014a; Zainuddin et al., 2019).

Overall, polymers are widely used in nano-enabled herbicide formulations due to their biodegradability and biocompatibility (Shakiba et al., 2020). For instance, poly(ε-caprolactone) (PCL) nanoparticles were developed primarily for atrazine (ATZ) (Grillo et al., 2012; Kah et al., 2014; Oliveira et al., 2015b; Sousa et al., 2018; Bombo et al., 2019; Zhai et al., 2020; Takeshita et al., 2021), metribuzin (MTZ) (Boyandin and Kazantseva, 2021), and ametryn (Clemente et al., 2014). Furthermore, synthesis of biopolymer-based nanocarriers for herbicide, such as chitosan (CS), was reported using chemical crosslinking agents (e.g., tripolyphosphate (TPP) (Grillo et al., 2014; Jacques et al., 2017; Paulraj et al., 2017), or functionalization with molecules such as 11-mercapto undecanoic acid (MUA) or N-octyl derivatives (Yu et al., 2015; Kamari and Yusoff, 2019). Chitosan functionalization and bioconjugation may be the keys to discovering excellent nano-enabled herbicides as well (Mohammadi et al., 2021). Hence, chitosan nanoparticles were reported with paraquat (PQ) (Silva et al., 2011; Grillo et al., 2015; Moreno et al., 2018; Rashidipour et al., 2019; Dong et al., 2021b; Pontes et al., 2021), glyphosate (Rychter, 2019), imazapic, imazapyr (Maruyama et al., 2016), and clomazone (de Oliveira et al., 2016). Also, copolymers such as poly(lactic-co-glycolic acid) (PLGA) can serve as potential nano-enabled herbicides due to the ability to manipulate their degradation in the environment (Tong et al., 2017; Schnoor et al., 2018).

Other efficient biopolymers for herbicide delivery are lignocellulosic materials such as lignin and nano/cellulose (Kumar et al., 2014; Lima et al., 2021; Yin et al., 2021). Moreover, pectin, a lignocellulosic material located in plants' primary cell walls, demonstrates a good acceptor for metsulfuron methyl herbicide (Kumar et al., 2017a). Pectin can also form blends with smaller molecules such as essential oils (Taban et al., 2021), which may have herbicidal activity. Furthermore, essential oils can be blended into gums/gelatin or nano-emulsified as a herbicide with an oil/water solution (Hazrati et al., 2017; Taban et al., 2020).

Table 1
Examples of organic nano-enabled herbicides and their main findings for weed control.

Nanoherbicide	Plant	Findings	Ref
PCL_ATZ NPs; PCL_Ametryn NPs; PCL_Simazine NPs;	*Allium cepa* L.	PCL NPs loaded herbicide showed less toxicity than free a.i.	(Grillo et al., 2012)
Nanoemulsion containing glyphosate	None	The system improved the bioactivity and bioavailability of the herbicide.	(Lim et al., 2012)
PCL_ATZ NPs	None	Good stability after 30 days and high encapsulation efficiency ~90%.	(Souza et al., 2012)
Nanoemulsion containing glyphosate	*Eleusine indica* (L.) GaertnGaertn	Size < 200 nm; Good biological effectiveness.	(Jiang et al., 2012)
CS_Alginate NPs	None	Low soil sorption, which improved its availability for herbicidal action.	(Silva et al., 2012)
Dendrimer_glyphosate	*Chlamydomonas reinhardtii Dangeard*	Nanoherbicide showed toxic effect to algae.	(Petit et al., 2012)
Nanoemulsion containing glyphosate	*Asystasia gangetica* (L.) T. Anderson; *Diodia ocymifolia* (Willd.) Bremek.; *Paspalum conjugatum* Berg	Improved uptake of herbicides in plants and reduced dosage.	(Lim et al., 2013a)
Carbon nanotubes_Diuron	*Chlorella vulgaris Beij*	The system was partially toxic to the algae, and the photosynthetic yield was not altered.	(Schwab et al., 2013)
PCL_ATZ NPs; PCL_Ametryn NPs	*Pseudokirchneriella subcapitata (Korshikov) F. Hindak*	The nanoformulations showed lower toxicity than the commercial ones.	(Clemente et al., 2014)
CS/TPP_PQ NPs	*Allium cepa* L.; *Zea mays* L.; *Brassica sp.* L.	Reduced herbicide toxicity; however, herbicide activity was maintained.	(Grillo et al., 2014)
PCL_ATZ NPs	*Brassica sp.*; *Zea mays* L.; *Allium cepa* L.	The nanoformulation was effective against target organisms, and it did not cause impact to the non-target organism.	(Pereira et al., 2014)
NC (BMA_DAAM) Acetochlor	*Alopecurus aequalis* Sobol; *Polypogon fugax* Nees	Size ~100 nm with good effectiveness in controlling weeds.	(Guo et al., 2014b)
PCL_ATZ NPs	None	Nanoherbicides may have different sorption on the soil.	(Kah et al., 2014)
Carboxymethyl Cellulose NC_ clodinafop-propyrgyl	None	Nanoherbicide showed slow release, herbicidal efficacy and low toxicity.	(Kumar et al., 2014)
CS/TPP_PQ NPs	*Allium cepa* L.; *Pseudokirchneriella subcapitata (Korshikov) F. Hindak*	Humic substances reduced toxic effects of the nanoherbicide for algae.	(Grillo et al., 2015)
SLN_Simazine; SLN_ATZ	*Raphanus raphanistrum* L.; *Zea mays* L.	The nanoformulations did not cause toxicity in non-target organisms; SLN showed phytotoxicity in shoots and roots of target plants.	(de Oliveira et al., 2015)
PCL_ATZ NPs	*Zea mays* L.	The nanoformulations caused transient effects such as a reduction in the maximum quantum yield of photosystem II and an increase in lipid peroxidation.	(Oliveira et al., 2015b)
PCL_ATZ NPs	*Brassica juncea (L.) Czern*	Reduction of photosynthesis and maximum quantum yield of photosystem II.	(Oliveira et al., 2015a)
Biochar_2,4-D	*Brassica sp.*; *Zea mays* L.	The nanoformulation did not cause toxicity in the non-target plant. However, it was lethal to *Brassica* sp. with an increase in herbicidal activity.	(Abigail et al., 2016)
CS/TPP NPs CS/Alginate NPs	*Bidens pilosa* L.; *Allium cepa* L.	Reduction of genotoxicity and toxicity at low concentrations.	(Maruyama et al., 2016)
Microemulsion of pretilachor	*Echinochloa crus-galli (L.) P. Beauv.*	The nanoherbicide increased the herbicidal effect.	(Kumar et al., 2016)
2,4-D-NBA-PEG	None	Development of photoresponsive micelles with slow release under solar irradiation.	(Ding et al., 2016)
Nanoemulsion_garden sarvori (*Satureja ortensis*) essential oil	*Amaranthus retroflexus* L.; *Chenopodium album* L.	Reduced germination, seedling growth, and weed chlorophyll content.	(Hazrati et al., 2017)
Pectin NPs_ metsulfuron methyl	*Chenopodium album* L.	Good herbicidal activity even in low doses of a.i., and low toxicity effect.	(Kumar et al., 2017a)
Guar gum nanohydrogel	*Coronopus didymus* (L.) Smith; *Melilotus indica* (L.) All; *Chenopodium album* L.; *Avena sterilis ssp.ludoviciana* Dur; *Phalaris minor Retz*	Controlled release system; Reduction in weed populations.	(Kumar et al., 2017b)
PCL_ATZ NPs	*Bidens pilosa* L.; *Amaranthus viridus* L.	Reduction in photosystem II activity and inhibition of plant growth.	(Sousa et al., 2018)
PLGA_ATZ NPs	*Solanum tuberosum* L.	Effective in inhibiting plant growth with low toxicity.	(Schnoor et al., 2018)
PMMA_Haloxyfop-R-metil NPs	*Lemna minor* L.	The nanoherbicide showed lower toxicity on the macrophyte compared to the non-encapsulated.	(Torbati et al., 2018)
Biochar_2,4-D	*Brassica* sp.; *Zea mays L.*	The system showed sustained release for ~26 days and good herbicidal activity.	(Abigail, 2019)
PMMA_Haloxifop-R-metil NPs	None	Nanoherbicide showed average diameter of 100–300 nm, ~95% encapsulation efficiency and slow release kinetic profile.	(Mahmoudian et al., 2020)
PLGA_ATZ NPs	None	The size distribution and encapsulation efficiency of the a.i. were from 204 to 520 nm and 31.6 to 50.5%, respectively.	(Chen and Wang, 2019)

(*continued on next page*)

Table 1 (*continued*)

Nanoherbicide	Plant	Findings	Ref
PCL_MTZ NPs	*Portulaca oleracea* L.; *Glycine max* (L.) Merr.	The nanoherbicide maintained its herbicidal activity for target plants.	(Diyanat and Saeidian, 2019)
PCL_Pretilachlor NPs	*Echinochloa crus-galli (L.) P. Beauv; Oryza sativa L.*	Nanoherbicide increased herbicidal activity with low toxic effect.	(Diyanat et al., 2019)
NOOSC_ATZ NONSC_ATZ NOOGC_ATZ	None	Encapsulation efficiency > 90%; controlled release of the herbicide atrazine.	(Kamari and Yusoff, 2019)
Nanoemulsion_palm oil and *Parthenium hysterophorus* L. crude extract	*Diodia ocymifolia* (Willd. ex Roem. & Schult.) Bremek	Inhibition of seed germination due to small particle size.	(Zainuddin et al., 2019)
PCL_ATZ NPs	*Brassica juncea* (L.) Czern	The nanoformulation showed herbicidal activity at low concentrations.	(Bombo et al., 2019)
CS/TPP_PQ NPs	None	DLS, PDI and potential zeta were ~ 150 nm, < 0,4, > 20 mV.	(Moreno et al., 2018)
Nano-hydrogels_CS	*Zea mays L.; Brassica* sp.	Good herbicidal activity for the target specie, and low toxicity for the non-target.	(Ghaderpoori et al., 2020)
Micelles_CS_2,4-D	*Cucumis sativus* L.; *Triticum aestivum* L.	Good herbicidal activity for the target specie, and low toxicity for the non-target.	(Feng et al., 2020)
NCs_savory (*Satureja ortensis* L.) essential oil	*Lycopersicon esculentum* Mill.; *Amaranthus retroflexus* L.	Nanoherbicide showed good herbicidal activity, causing a reduction of photosynthetic pigments in plants.	(Taban et al., 2020)
PCL_ATZ NPs	*Bidens pilosa L.; Glycine max L.*	NC_ATZ increased the herbicidal activity against weed species.	(Preisler et al., 2020)
Nano-hydrogel_ glyphosate	Weeds; *Oryza sativa* L.	Nanoherbicides reduced the impact on non-target species and improved herbicidal activity.;	(Zhang et al., 2020)
QNC-EB-COFs	*Echinochloa crusgalli* (L.) P. Beauv	Sustained release and good herbicidal activity against weeds.	(Deng et al., 2021)
NCEs	*Amaranthus retroflexus L.; Solanum lycopersicum* L.;	The phytotoxic capacity caused a reduction in germination and plant weight.	(Taban et al., 2021)
PCL_Metribuzin NPs	None	Nanoherbicide showed a long-term release of ~81–96% during seven days.	(Boyandin and Kazantseva, 2021)
Nano_hydrogel_Dicamba	None	Nanoherbicide showed a sustained release for 10 days.	(Artusio et al., 2021)
PCL_ATZ NPs	*Brassica juncea* (L.) Czern.	Nanoformulation reduced the activity of photosystem II at low doses of the a.i..	(Takeshita et al., 2021)
PCL_ATZ NPs	*Lactuca sativa L.*	Nanoformulation inhibited lettuce growth in a short-term exposure, and induced adverse effects in the long-term.	(Wu et al., 2021)
NSs_Ailanthone	*Lepidium sativum* L.; *Raphanus sativus* L.	Nanoherbicide reported prolonged release of the a.i., and increased its herbicidal activity.	(Demasi et al., 2021)
Carbon nanotubes_Glyphospate	*Arabidopsis thaliana* L.	Nanoherbicide exhibited changes in plant growth and photosynthetic apparatus of the plant.	(Ke et al., 2021)
Nanoemulsion_*Foeniculum vulgare* essential oil	*Phalaris minor Retz; Avena ludoviciana Durieu; Rumex dentatus* L.; *Medicago denticulata* Willd.	Low-dose of nanoemulsions inhibited plant germination, affecting physiological processes.	(Kaur et al., 2021)
CS/TPP_PQ NPs	*Spinacia oleracea* L.	The nanoherbicide maintained the herbicidal activity of paraquat.	(Pontes et al., 2021)
Microemulsion_TM	*Convolvulus arvensis* L.	The nanoformulation exhibits herbicidal activity at low concentrations of a.i..	(Heydari et al., 2021b)

Acronyms: Butyl methacrylate (BMA); Diacetone acrylamide (DAAM); Polydispersity index (PDI); Dynamic light scattering (DLS); Optimized diuron nanoformulation (ODNF); Nanostructured liquid crystalline particles (NLCP); 3-nitro-4-bromomethylbenzoic acid- Polyethylene glycol (NBA-PEG); Poly(methyl methacrylate) (PMMA); *N*-octyl-*O*-sulfate chitosan (NOOSC); *N*-octyl-*N*-succinyl chitosan (NONSC); *N*-octyl-*O*-glycol chitosan (NOOGC); quinclorac (QNC); Ethidium bromide-based covalent organic frameworks (EB-COFs); Nano-encapsulated essential oils (NCEs); Dextrin-based nanosponges (NSs).

On the other hand, proteins are ascending in the formation of organic nano-enabled herbicides, with zein being the pioneer. Zein is a plant protein and can be a nanocarrier to carry out bioactives like tribenuron-methyl (TM) (Heydari et al., 2021a). Other organic molecules include perylene-3-ylmethanol, rice husk derivatives, polydopamine, and phytantriol (3,7,11,15-tetramethyl1,2,3-hexadecanetriol), which can also be used as nanocarriers for herbicide (Atta et al., 2015; Abigail et al., 2016; Abigail, 2019; Shen et al., 2019). In addition, organic nano-enabled herbicides can range in design from nanocapsules to nanosponges (Demasi et al., 2021). Some examples of these types of nanoherbicide can be seen in Table 1.

2.2. Inorganic nano-enabled herbicides

Inorganic nano-enabled materials are increasingly being investigated for agricultural applications in order to improve crop yield and herbicidal performance, resulting in waste reduction and runoff (Cartwright et al., 2020). Inorganic nano-enabled herbicides can be based on silica (Ghazali et al., 2021a), metal (Wen et al., 2016; Ke et al., 2018), mesoporous silica nanoparticles (Cao et al., 2018), etc. Some of these nanoherbicides can release ions, while others can encapsulate organic molecules and release them in a controlled manner. For instance, inorganic nanoformulations based on double-layer zinc/aluminum hydroxides (Hussein et al., 2005; Sharif et al., 2020c), or magnesium-aluminum associated with sepiolite clay (Rebitski et al., 2019), have been widely used for herbicide association since they may delay herbicide leaching through the soil (Hussein et al., 2005; Hussein et al., 2010; Sarijo et al., 2015; Ghazali et al., 2021b) and improve the transport of active ingredients to the plant (Rebitski et al., 2019). Also, these systems can encapsulate hydrophobic herbicides between their layers and be used to combat *Chlamydomonas reinhardtii Dang* algae (Touloupakis et al., 2011). On the other hand, clay minerals can

Table 2
Examples of inorganic nano-enabled herbicides and their main findings for weed control.

Nanoherbicide	Plant	Findings	Ref
Zn-layered hydroxide (ZLH)_DBPA_CPPA	None	PXRD and FTIR analyzes showed the intercalation of herbicides. The proportion of CPPA and DBPA interleaved in ZLH is ~ 16.22% and 83.78% (w/w).	(Hussein et al., 2012b)
Zn-layered hydroxide (ZLH)_4CPA	None	PXRD and FTIR analyzes showed the intercalation of herbicides, and the loading capacity was ~ 45.4% (w/w)	(Hussein et al., 2012a)
Zn-Al-MCPA-layered double hydroxide	None	PXRD and FTIR analyzes showed the intercalation of herbicide. Size of ZAL and ZAM was ~ 115 and 128 nm; MCPA loading capacity was ~ 45% (w/w).	(Sarijo et al., 2013)
Zn-Al-TBA-layered double hydroxide	None	PXRD and FTIR analyzes showed the intercalation of herbicide. TBA loading capacity was ~ 45.5% (w/w).	(Ghazali et al., 2014)
Hal_AMT Kaol_AMT	None	The formulation showed slow release of AMT, and the loading capacity was ~30.5% and 20.8% to the methoxy-modified Hal and Kaol, respectively.	(Tan et al., 2015a)
SMSs NPs_2,4-D	None	Formulation with the potential to slow release 2,4D herbicide.	(Bhardwaj et al., 2015)
Zn-Al-layered double hydroxide (ZAL) _MCPA_3,4D	None	PXRD, DIMS, and FTIR analyzes showed the intercalation of herbicide. MCPA and 3,4D loading capacity were ~13.4% and 28.3% (w/w).	(Sarijo et al., 2015)
AMT_Kaol$_{(MeOH)}$	None	The AMT loading in the methoxy-modified Kaol was ~ 20.8% (w/w), and the average diameter of the crystallites was 33.4 nm.	(Tan et al., 2015b)
Zn-Al-layered double hydroxide (ZAL) _CPA Zn-Al-layered double hydroxide (ZAL) _DPA Zn-Al-layered double hydroxide (ZAL) _DCPA	None	PXRD, DIMS, and FTIR analyzes showed the intercalation of herbicides. Promising system for the controlled release of more than one herbicide at the same time.	(Bashi et al., 2012)
HNTs-AT	None	The herbicide showed slow release profile compared to the free a.i.; FTIR and TEM analyzes evidenced the encapsulation of atrazine herbicide.	(Zhong et al., 2017)
Zn-Al-layered double hydroxide (ZAL) _BNOA	None	PXRD, and FTIR analyzes showed the intercalation of herbicide. The BNOA loading capacity was ~36.2% (w/w).	(Jubri et al., 2017)
Mesoporous silica NPs_TA_2,4-D	*Cucumis sativus* L.; *Triticum aestivum* L.	Good herbicidal bioactivity on target plant.	(Cao et al., 2018)
Layered double hydroxide (LDH)_Imz	*Brassica nigra (L.) W.D.J. Koch*	Nanoherbicides inhibited plant growth while maintaining its herbicidal activity.	(Khatem et al., 2019)
Clay-imazaquin	*Brassica oleracea var. botrytis* (L.)	Increased effectiveness of herbicidal activity.	(López-Cabeza et al., 2019)
Mg-Al-layered double hydroxide (ZAL) _2,4-D	*Arabidopsis thaliana* (L.) Heynh	Nanoclay applied in higher concentrations induced the formation of callose.	(Nadiminti et al., 2019)
Nanoclay_2,4-D	None	The release profile showed an initial fast release followed by a slow release.	(Natarelli et al., 2019)
DQ@MSN-SO$_3$	*Datura stramonium* L.	Stimulus-responsive delivery system. The nanoparticles showed good herbicidal activity.	(Shan et al., 2019)
HNTs-AIEAS	None	Nanoherbicides showed good herbicidal capacity and slow release profile of the a.i.	(Zeng et al., 2019)
Mg-Al-layered double hydroxide (ZAL) _2,4-D	None	XRD analysis showed the intercalation of the herbicide, and controlled release of the herbicide.	(Rebitski et al., 2019)
ZHN-SDS-BP	*Oryza sativa* L.	FTIR, XRD, and ICP-OES analyzes showed herbicide intercalation, and low release of the herbicide.	(Sharif et al., 2020a)
NF-sepiolite_MS	*Zea mays* L.; *Helianthus annuus* L.	Nanoformulation with the same bioactivity in the field compared to the commercial formulation.	(Galán-Jiménez et al., 2020)
Zn-Al-layered double hydroxide (ZAL)_CP	None	PXRD, and FTIR analyzes showed herbicide intercalation.	(Sharif et al., 2020c)
Herbicide@HTlcs	*Amaranthus retroflexus*	HTlcs showed a potential herbicidal property.	(Gao et al., 2021)
TMZNP-5	*Convolvulus arvensis* L.	TMZNP-5 showed the same effectiveness as the commercial formulation at low concentrations.	(Heydari et al., 2021a)
Zn-Al-layered double hydroxide (ZAL) _TBA_MCPA	None	PXRD, FTIR, and FESEM analyzes showed the intercalation of the anions.	(Ghazali et al., 2021a)
Zn-Al-layered double hydroxides_TBA_3,4-D	None	Formulation with controlled release of the a.i.	(Ghazali et al., 2021b)

Acronyms: 2-(3-chlorophenoxy) propionate (CPPA); 4-(2,4-dichlorophenoxy) butyrate (DPBA); 4-Chlorophenoxy acetate (4CPA); 2-methyl-4-chlorophenoxyacetic acid (MCPA); 2,4,5-tricholorophenoxybutyrate (TBA); Halloysite (Hal); Kaolinite (Kaol); Amitrole (AMT); Nanoparticles (NPs); Surfactant modified silicates (SMSs); 2,4-Dichlorophenoxyacetic acid (2,4-D); 3,4-dichlorophenoxyacetate (3,4-D); Silver (Ag); Imazethapyr (IM); 2,4-dichlorophenoxy acetate (DPA); Halloysite nanotubes (HNTs); beta-naphthoxyacetate (BNOA); Trimethylammonium (TA); Imazamox (Imz); Diquat dibromide (DQ); Active ingredients of *eupatorium adenophora* spreng (AIEAS); Zinc hydroxide nitrate (ZHN); Sodium dodecylsulphate (SDS); Bispyribac (BP); Nanoformulation (NF); Mesotrione (MS); Clopyralid (CP); Hydrotalcites (HTlcs); Tribenuron-methyl zein-based nanoparticles (TMZNP-5); X-ray powder diffraction patterns (PXRD); Fourier transform infrared (FTIR); Direct-injection mass spectroscopy (DIMS); Field emission scanning electron microscopy (FESEM); Inductively coupled plasma optical emission spectrometry (ICP-OES); Transmission electronic microscopy (MET).

potentially form nano-enabled herbicides since they can be biocompatible, cheap, and have good scalability (Lima et al., 2022). For instance, hydrotalcite nanosheets associated with herbicide showed better physicochemical stability and herbicidal activity than conventional ones (Gao et al., 2021). Furthermore, mesoporous silica nanoparticles (MSN) are used as herbicide carriers due to their response to pH and strong electrostatic interactions (Cao et al., 2018; Shan et al., 2019). Some examples of inorganic nanoherbicides can be shown in Table 2.

2.3. Hybrid nano-enabled herbicides

Hybrid materials have the potential to combine the advantages of two or more materials, such as organic and inorganic, into a single structure (Gao et al., 2020). These multifunctional nanomaterials can have a variety of properties, sizes, morphologies, and chemical compositions (Aich et al., 2014; Ananikov, 2019). Also, hybrid nanoherbicides can promote good targetability, traceability, and stimuli-responsiveness property (Chen et al., 2018a; Zhao et al., 2020; Li et al., 2021).

Biomass-based hybrids constituted by lignin, xylan, starch, and cellulose have been studied to encapsulate active molecules and be used in the targeted delivery of herbicides due to properties such as biocompatibility, biodegradability, and characteristics such as natural abundance and easy functionalization (Mahajan et al., 2021). For instance, the synthesis of hybrid xylan-lignin nanoparticles gives the nanomaterial amphiphilic properties and forms a core-shell structure (Jiang et al., 2020). In addition, lignin-based derivatives can be combined with inorganic substances such as copper salts, producing antibacterial and antifungal materials (Sinisi et al., 2019). Furthermore, organic-inorganic nanohybrids containing copper oxide nanoparticles show good antimicrobial activity (Almasi et al., 2018) and can be potential materials for weed control.

Inorganic mineral materials can also serve as hybrid nano-enabled herbicide, for example, natural clay and biopolymers have a great affinity with a wide range of pesticides that may be improved through chemical modifications (Granetto et al., 2022). Also, iron can also be associated with other inorganic materials such as montmorillonite (Mt) clay to design hybrid nanoherbicides (Marco-Brown et al., 2012) with excellent sorption capacity (Marco-Brown et al., 2017; Xiang et al., 2017). Thus, iron oxide NPs can confer a superparamagnetic property while promoting a responsive release as reported by Chi et al. (2021). Moreover, superparamagnetic iron oxide nanoparticles (SPIONs) associated with nanocomposites can promote intelligent nanocarriers for cargo delivery (Forini et al., 2020; Grillo et al., 2016), which can release a.i. under an external magnetic field.

In addition, metal-organic frameworks (MOFs) are emerging structures that can act as suitable carriers for the controlled release of herbicides since they have different properties, such as versatile hybrid compositions, large surface areas, and good stability (due to their porous structure) (Lee et al., 2022; Rojas et al., 2022). The encapsulation of herbicides in MOFs has a higher herbicidal activity when compared to the pure active ingredient since their transport mechanism can facilitate the assimilation by plant cells (Mejías et al., 2021).

Chemical interactions among different compounds can turn materials into excellent nano-enabled herbicide carriers. For instance, hydrophilic materials can be modified to encapsulate hydrophobic pesticide molecules (Hao et al., 2020a). Hence, with better spreadability, better leaf adhesion, and less UV irradiation degradation, hybrid nanocarriers are becoming more effective in encapsulating herbicides. These outcomes shape nanoherbicides as strong candidates in the journey of sustainable agriculture (Zhao et al., 2020; Hao et al., 2020b). Some examples of hybrid nanoherbicide can be shown in Table 3.

3. Nano-enabled herbicides can enhance the herbicidal activity

When compared to commercial formulations, the novel properties of nanoherbicides can lead to new mechanisms of biological interactions and improve herbicidal activity. The ability of nanocarriers to enhance the effect of a.i. in plants (Mittal et al., 2020) has been demonstrated in previous studies using nanoherbicides in a variety of plant systems. Currently, some hypotheses have been proposed to explain this phenomenon. For instance, the ability of nanoencapsulation to protect the a.i. against physicochemical degradation, particularly over the long-term duration of field conditions, may be a great advantage associated with the use of nano-enabled herbicides (Mattos et al., 2017; de Oliveira et al., 2018). Additionally, the controlled and sustained release of chemical cargo over time is crucial for preventing its early physicochemical degradation and improving its efficiency by controlling the dissolution profiles of the herbicides (Mattos et al., 2017; Kah et al., 2018). This behavior is essential for the enhanced efficiency of nano-enabled herbicides.

The adhesion of post-emergent nanoherbicides to plant foliar tissues is currently attracting increasing interest. The leaves' outer layers, i.e., cuticle and epidermis, showed morphological and chemical composition differences according to plant species and environmental factors, such as temperature, humidity, and radiation (Barthlott et al., 2017; Lim et al., 2020; Stępiński et al., 2020). Leaf cuticles mainly consist of the amphiphilic long fatty acid-based polyester cutin and hydrophobic cuticular waxes, primarily located on the exterior side (Lim et al., 2020). The outer cuticular side is composed of cutin, and the inner cuticular side is composed of polysaccharides (Ziv et al., 2018). Thus, herbicides loaded into hydrophobic nanocapsules might show a better interaction with the leaf cuticle, for instance, increasing the delivery of a.i. to the plant target tissues (Avellan et al., 2019; Grillo et al., 2021b; Yang et al., 2021). Nonetheless, the cuticular uptake pathway is a potential route for nanopesticides' entrance into the leaves. Given the superior cuticle area on the leaf surface compared to the stomata area, the cuticle may be a more effective pathway for nanoherbicide adhesion and entry into the leaf (Fig. 2**-A**). Depending on the chemical nature of the nanoherbicides, the cuticular entrance of nano-enabled herbicides in the leaf may occur through small pores (pore pathway), cuticle diffusion or disruption (direct pathway), or both cases (Fig. 2**-B**).

In modern agriculture systems, the spraying process for conventional herbicide applications fails to target plant foliage. Some issues may arise during this process, such as droplet drifting, jumping, rolling down, rain washing, and herbicide decomposition (Zhao et al., 2018; Song et al., 2019; Shen et al., 2022). Herbicide wettability and retention on the surface of weed foliage are critical factors for improving herbicide deposition, adsorption, adhesion, and performance. Improving leaf surface adhesion with nanoherbicides has the potential to extend herbicide duration on weed leaves and improve utilization efficiency. Thus, literature reports that nanoherbicides provide better adhesion to plant foliage (Yu et al., 2017; Zhao et al., 2018). For instance, it was feasible to modulate leaf adhesion and optimize herbicidal absorption and efficiency depending on the type and composition of the nanoherbicide. Also, the formation of H-bonding involving phenolic OH and the leaf surface may induce better leaf adhesion and high persistence of nanopesticides on the leaf surface (Grillo, et al., 2021b). Another important factor is the surface charge of nanopesticides, which directly affects the interactions of nanopesticides with different biological components, such as proteins and carbohydrates (Tripathi et al., 2017).

Additionally, physicochemical properties of nanoherbicides such as the size, morphology, and surface charge of nanoherbicides **(**Fig. 2**-C)** are important traits related to the foliar adhesion, uptake, internalization, and action of nanoherbicides in plant tissues (Grillo et al., 2021b; Takeshita et al., 2021). Nanoherbicides with a size range of around $<$ 100 nm can easily disrupt the cuticle waxy layer and penetrate through the plant cuticle (Larue et al., 2014). The surface charge of nanoherbicide is another important factor, mainly due to their activity as membrane disruptors by affecting proton motion force and facilitating intracellular transport (Shekhar et al., 2021). Therefore, a deeper understanding of how nanoherbicides' physiochemical properties contribute to their enhanced herbicidal action is essential for creating new, more effective nanoherbicides.

New studies are currently in progress involving nanoherbicides to investigate their enhanced herbicidal effects. For instance, nanoformulations containing herbicides have demonstrated pre-and post-emergence herbicidal effects. On cucumber plants, mesoporous silica loaded with 2, 4-D herbicide exhibited excellent inhibition behavior

Table 3
Examples of nano-enabled organic/inorganic hybrid herbicides and their main findings for weed control.

Nanoherbicide	Plant	Findings	Ref
Fe_3O_4 NPs coated with hollow silica spheres_glyphosate	None	Size < 100 nm; The herbicide release rate was affected by the shell thickness of the hollow silica spheres.	(Liu et al., 2012)
WG_C30B_ethofumesate	None	Nanoherbicide reported slow release of the a.i., and reduced the amount of herbicide available in the medium.	(Chevillard et al., 2012)
AgNPs_CS_PQ	*Eichhornia crassipes (Mart.) Solms*	The nanoformulation did not affect plant germination and growth.	(Namasivayam et al., 2014)
Starch-clay (MMT) nanocomposite_AMT	None	SEM and XRD analyzes showed an amorphous structure of the nanocomposite, and intercalation of the herbicide.	(Giroto et al., 2014)
WG_C30B_ethofumesate	*Lepidium sativum* L.	The nanoherbicide reduced watercress germination; and it showed a promising system to protect pesticides from photodegradation.	(Chevillard et al., 2014)
GSNO-containing alginate/chitosan nanoparticles	*Zea mays L.; Glycine sp.* Willd	The nanoherbicide had no effect on the growth and development of the species studied.	(Pereira et al., 2015)
SWFe–Imx SWCS-Imx	*Brassica oleracea* var. *botrytis* L.	Nanoherbicide reported a reduction of herbicide release rate, and showed similar herbicidal activity to commercial ones.	(Cabrera et al., 2016)
PRCRP@ Fe_3O_4 NPs_CS	*Cynodon dactylon* (L.) Pers	Nanoherbicide with pH-responsive release and good herbicidal activity.	(Xiang et al., 2017)
ATP-NH_4CO_3-Gly – ASO – PVA	*Zoysia matrella* (L.) Merr.	Nanoformulation showed good herbicidal activity	(Chi et al., 2017)
Clay/Alg/PQ	None	The nanoformulation showed an initial fast release followed by a slow release of the a.i.	(Rashidzadeh et al., 2017)
LCHP	*Imperata cylindrica* (L.) Raeusch	Light-responsive controlled release; the nanoherbicide was effective to control weeds due its high adhesion on the leaf surface.	(Chen et al., 2018a)
ONCHP	*Cynodon dactylon* (L.) Pers.	Light-responsive controlled release nanoherbicide showed a good weed control.	(Liu et al., 2019)
Zn/Al-LDH-QC-CS	None	The nanoherbicide showed a slow release of the a.i., and FTIR, XRD, and TGA/DTG analyzes evidenced the chitosan coating.	(Sharif et al., 2020b)
MLH-MPP/CMC	None	FTIR, TEM, and SEM analyzes showed herbicide intercalation, and the nanoherbicide reported a controlled release system of the a.i..	(Hashim et al., 2020)
MCRH	*Cynodon dactylon* (L.) Pers	The release of the herbicide was accelerated in the presence of a magnetic field. Also, the nanoformulation had the same weed control of the commercial ones.	(Chi et al., 2021)
Zn/Al-LDH-QC-CMC	None	The system showed a prolonged release profile to the herbicide.	(Sharif et al., 2021)
MOF@DiS – NH_2 MOF@DiS – *O* - acetil	*Lolium rigidum* Gaudin; *Echinochloa crus-galli* (L.); *Amaranthus Viridis L.*	Nanoformulation reported phytotoxic activity against weeds.	(Mejías et al., 2021)

Acronyms: Wheat gluten (WG); Organically modified montmorillonite (C30B); montmorillonites (MMT); Ametryne (AMT); nitrosoglutathione (GSNO:S); natural smectite (SW); Imazamox (IMX); pH-responsively controlled-release nanopesticide (PRCRP); Scanning electron microscope (SEM); Alginate (ALG); Light-responsively controlled-release herbicide particle (LCHP); Near-infrared light (NIRL)-responsively controlled-release herbicide particles (ONCHPs); Quinclorac (QC); thermo-gravimetric analysis (TGA); 3-(4-methoxyphenyl) propionate (MLH-MPP); Carboxymethylcellulose (CMC); Magnetic-responsive controlled-release herbicide; MOFs:Metal–organic frameworks (MCRH); Attapulgite (ATP); Amino silicol oil (ASO); poly(vinyl alcohol) (PVA).

(Cao et al., 2018). The same herbicide loaded into lipid nanoparticles and perylen-3-ylmethanol nanoparticles showed enhanced herbicidal effects in low doses compared with a free a.i. (Atta et al., 2015; Nadiminti et al., 2016). Aerial and root growth is significantly inhibited by atrazine-simazine loaded onto solid lipid nanoparticles (de Oliveira et al., 2015). In another study using Cogon weeds, their growth was better inhibited by chitosan/carboxymethyl nanoparticles carrying diuron (Chen et al., 2018a). It is important to note that the chemical properties of nanoherbicides play a crucial role in their interaction with plant leaves, roots, and seed tissues, their path of entry and cellular fate, and subsequently their target effects.

4. Fate and behaviour of nanoherbicides in plant systems

There are still few experimental studies that focus on the fate and behavior of these nanoherbicides rather than the physiological, metabolic, and biochemical mechanisms involved in plant responses. However, other researchers reported that nanopesticides altered plant gene expression and caused changes in lipid peroxidation, chlorophyll content, protein content, and enzymatic/non-enzymatic antioxidant activity (Zhao et al., 2016; Zhang et al., 2019; Pontes et al., 2021; Wu et al., 2021; Oliveira-Pinto et al., 2022). After overcoming biological barriers to entry into a plant cell, nanoherbicides may damage or disrupt the cell membrane of target species and induce electrolyte leakage into the extracellular medium (Jambunathan, 2010) and lipid peroxidation (Oliveira et al., 2015a). Studies have shown that a mechanism adopted by plants to alleviate stress-induced damage by nanomaterial cell internalization is the compartmentalization of nanostructures into vacuoles (Panariti et al., 2012). Additionally, nanoherbicides may go to plant organelles and induce changes in their functioning (Pérez-de-Luque, 2017; Mittal et al., 2020). For instance, in plant cells, the mitochondrial electron transport chain (ETC) is an important site of reactive oxygen species (ROS) production, followed by chloroplast ETC (Huang et al., 2016). Previous research has found both enzymatic and non-enzymatic antioxidant activity in response to ROS generation (Oliveira et al., 2015a; Pontes et al., 2021; Wang et al., 2022a). The key factors involved in nanoherbicides' induced ROS can include: (i) prooxidant functional groups attached to the reactive surface of nanoherbicide; (ii) active redox cycling on the surface of nanoherbicide, especially in hybrid (metal or metal oxide nanoparticles-labeled) formulations due to the transition of these nanomaterials; and (iii) particle or cargo-cell interactions (Manke et al., 2013). Nonetheless, more studies are needed to better comprehend the mitochondrial fate of nanoherbicides, mainly focusing on the tricarboxylic acid (TCA) cycle (Wang et al., 2021). Additionally, in the chloroplast, some nanoherbicides induce a decrease in quantum yield of photosystem II (PSII), photosystem I (PSI) deactivation, ferredoxin-NADP+ oxidoreductase (NADPH/NADP+ ratio), and net CO2 assimilation rate (Oliveira et al.,

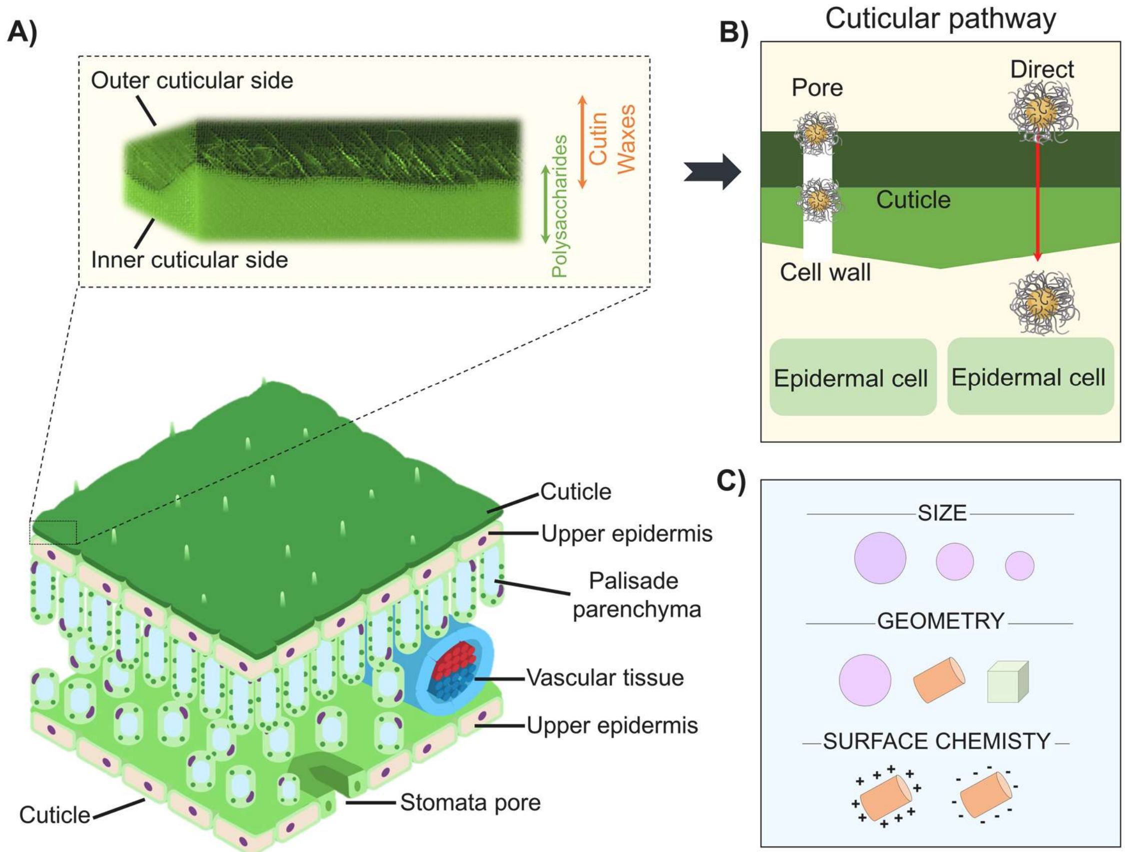

Fig. 2. A) Schematic representation of the anatomy of a leaf structure. B) Potential cuticular pathway for uptake nanoherbicides by leaf. C) Some important physicochemical characteristics of nanoherbicides.

2015b; Forini et al., 2020; Pontes et al., 2021; Takeshita et al., 2021).

In the plant cell nucleus, genotoxicity evaluation in *Allium cepa* cells showed that the herbicides imazapic and imazapyr encapsulated with chitosan/tripolyphosphate and alginate/chitosan nanoparticles caused minor damage compared to the free a.i. (Maruyama et al., 2016). Polycaprolactone nanocapsules (PCL) containing pre-emergent herbicide pretilachlor indicated that the presence of PCL nanoencapsulation acted to reduce the toxicity of the herbicide due to a reduced effect on chromosome aberration in *Allium cepa* (Diyanat et al., 2019). Nanopesticides may damage genetic materials if they penetrate inside the cellular nucleus and come into direct contact with DNA molecules or proteins associated with DNA (Singh et al., 2009). In addition, nanoherbicides can up-regulate the expression of antioxidant-related genes (Wang et al., 2022b). Hence, nano-enabled agriculture requires further attention to improve our understanding of the genotoxicity and transcriptomic behavior of nanoherbicides for target and non-target plant species.

The endoplasmic reticulum is responsible for protein and lipid production, and consequently, the possible fate of nanoherbicides. Decreases in protein synthesis are expected when nanoherbicides enter the endoplasmic reticulum. Additionally, when a nanomaterial enters a physiological environment, it rapidly adsorbs proteins, forming what is known as the protein corona (Walkey and Chan, 2012). These interactions are currently poorly studied for nanoherbicides, and more studies are necessary to improve our understanding of their responses. It can acquire a novel biological identity that is distinct from its synthesized form (Wheeler et al., 2021) owing to the nanoherbicide-protein corona.

Cell membranes internalize nanoherbicides via passive processes, i.e., passing through the membrane without transporter or cell energy, or via active processes, such as largely endocytic (Sun et al., 2019; Moore et al., 2022). Additionally, differentiated (i) nanocarrier-(ii) specific cargo uptake and/or cellular transport might occur. For instance, Moore and coauthors (2022) suggested the co-localization of the nanoherbicide into the membrane-rich Golgi-apparatus, in close proximity to the nucleus (Moore et al., 2022). These results revealed that conventional herbicides compared with nanoherbicides differ in uptake mechanisms and cellular dynamics (Gomes et al., 2022). After entry into cell membranes, nanoherbicides may be trafficked to diverse cell organelles.

Currently, most of the nanoherbicides developed and tested are formulated with cargo molecules of already known a.i. or even with nanoparticles that have been widely studied, which may explain the few experimental articles on the effects and pathways of action of nanoformulations on plant metabolism. However, nanoformulations, acquire novel properties that can affect how plants respond in various ways (Wu et al., 2021). Another important gap is the interaction of nanoherbicides with non-target plants and rhizosphere systems. As recently reported by Zhai et al. (2020) with nanoatrazine, nanoherbicides may have some distinct adverse effects on non-target plants and their rhizosphere bacterial communities, especially after long-term exposure. Thus, the plant-soil system relationship may play an important role in the safe application of nanoherbicides. Therefore, they deserve special attention regarding their mode of action and behavior in plant metabolism. Additionally, understanding the mechanism of action of an herbicide used as chemical cargo is essential to designing transgenic cultivars with specific resistance genes for novel nano-enabled herbicides.

5. Conclusion and future outlook

Recent nano-enabled herbicides have been used for weed management based on inorganic, organic, and hybrid materials. Studies have shown that nanoherbicides can produce more targeted and less toxic formulations for agricultural applications. However, the development of smart nanoherbicides as well as a better understanding of the mechanisms of action of nanoherbicides is needed to target and non-target organisms. Furthermore, it should be noted that the biological factors limiting the efficiency of nanomaterials-cargo complexes and nanomaterials traveling across barriers in plants may differ in diverse nanoformulation systems. In addition, future research is recommended to contribute to improving the knowledge of the mode of action of nanoherbicides. The number of agrochemicals needed can be decreased in the future with the development of innovative delivery platforms, such as herbicides co-loaded with CRISPR-based genome editing for simultaneous action on non-target plant tissues (Yan et al. 2022). Another important aspect of the development of novel nanoherbicides is the inability of current nanostructured delivery systems to precisely target specific subcellular compartments, particularly guided by biorecognition motifs as recently reported by Santana et al. (2020). This molecular target recognition needs to be improved for novel nanoformulations, and this can be supported using strategic design, artificial intelligence (AI), and machine learning concepts (Zhang et al., 2021). Thus, numerous investigations are still to be conducted, which may further the development of nanoherbicides to provide products for environmentally friendly and sustainable agriculture.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors acknowledge funding from National Council for Scientific and Technological Development, CNPq, Brazil (Grant no. #427498/2018-0 and #161360/2021-1), São Paulo Research Foundation, FAPESP, Brazil (Grant no. #2020/12769-0 and #2017/21004-5), and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior, CAPES, Brazil—Finance Code 001. The figure was partially created in the "Mind the Graph" platform (https://mindthegraph.com).

References

Abdollahdokht, D., Gao, Y., Faramarz, S., Poustforoosh, A., Abbasi, M., Asadikaram, G., Nematollahi, M.H., 2022. Conventional agrochemicals towards nano-biopesticides: an overview on recent advances. Chem. Biol. Technol. Agric. 9, 13. https://doi.org/10.1186/s40538-021-00281-0

Abigail, M.E.A., 2019. Biochar-based nanocarriers: fabrication, characterization, and application as 2,4-dichlorophenoxyacetic acid nanoformulation for sustained release. 3 Biotech 9, 317. https://doi.org/10.1007/s13205-019-1829-y

Abigail, M.E.A., Samuel M., S., Chidambaram, R., 2016. Application of rice husk nanosorbents containing 2,4-dichlorophenoxyacetic acid herbicide to control weeds and reduce leaching from soil. J. Taiwan Inst. Chem. Eng. 63, 318–326. https://doi.org/10.1016/j.jtice.2016.03.024

Aich, N., Plazas-Tuttle, J., Lead, J., Saleh, N., 2014. A critical review of nanohybrids: synthesis, applications, and environmental implications. Environ. Chem. 11. https://doi.org/10.1071/EN14127

Almasi, H., Jafarzadeh, P., Mehryar, L., 2018. Fabrication of novel nanohybrids by impregnation of CuO nanoparticles into bacterial cellulose and chitosan nanofibers:characterization, antimicrobial and release properties. Carbohydr. Polym. 186, 273–281. https://doi.org/10.1016/j.carbpol.2018.01.067

An, C., Sun, C., Li, N., Huang, B., Jiang, J., Shen, Y., Wang, C., Zhao, X., Cui, B., Wang, C., Li, X., Zhan, S., Gao, F., Zeng, Z., Wang, Y., 2022. Nanomaterials and nanotechnology for the delivery of agrochemicals: strategies towards sustainable agriculture. J. Nanobiotechnol. 20 (1), 1–19.

Ananikov, V.P., 2019. Organic-inorganic hybrid nanomaterials. Nanomaterials 9, 1197. https://doi.org/10.3390/nano9091197

Artusio, F., Casà, D., Granetto, M., Tosco, T., Pisano, R., 2021. Alginate nanohydrogels as a biocompatible platform for the controlled release of a hydrophilic herbicide. Processes 9. https://doi.org/10.3390/pr9091641

Atta, S., Bera, M., Chattopadhyay, T., Paul, A., Ikbal, M., Maiti, M.K., Singh, N.D.P., 2015. Nano-pesticide formulation based on fluorescent organic photoresponsive nanoparticles: for controlled release of 2,4-D and real time monitoring of morphological changes induced by 2,4-D in plant systems. RSC Adv. 5, 86990–86996. https://doi.org/10.1039/C5RA17121K

Avellan, A., Yun, J., Zhang, Y., Spielman-Sun, E., Unrine, J.M., Thieme, J., Li, J., Lombi, E., Bland, G., Lowry, G.V., 2019. Nanoparticle size and coating chemistry control foliar uptake pathways, translocation, and leaf-to-rhizosphere transport in wheat. ACS Nano 13, 5291–5305. https://doi.org/10.1021/acsnano.8b09781

Awad, M., Ibrahim, E.-D.S., Osman, E., Elmenofy, W.H., Mahmoud, A.W.M., Atia, M.A.M., Moustafa, M.A.M., 2021. Nano-insecticides against the black cutworm agrotis ipsilon (Lepidoptera: Noctuidae): toxicity, development, enzyme activity, and DNA mutagenicity. bioRxiv.

Barthlott, W., Mail, M., Bhushan, B., Koch, K., 2017. Plant surfaces: structures and functions for biomimetic innovations. Nano-Micro Lett. 9, 23. https://doi.org/10.1007/s40820-016-0125-1

Bashi, A., Hussein, M., Zainal, Z., Rahmani, M., Tichit, D., 2012. Simultaneous intercalation and release of 2,4-dichloro- and 4-chloro-phenoxy acetates into Zn/Al layered double hydroxide. Arab. J. Chem. 220. https://doi.org/10.1016/j.arabjc.2012.03.015

Bhardwaj, D., Sharma, P., Sharma, M., Tomar, R., 2015. Hydrothermally synthesized organo-silicate nanoparticles as adsorbent and slow release formulation of 2,4-dichlorophenoxyacetic acid (2,4-D). Environ. Eng. Manag. J. 14, 2887–2896. https://doi.org/10.30638/eemj.2015.306

Bocca, B., Barone, F., Petrucci, F., Benetti, F., Picardo, V., Prota, V., Amendola, G., 2020. Nanopesticides: physico-chemical characterization by a combination of advanced analytical techniques. Food Chem. Toxicol. 146, 111816. https://doi.org/10.1016/j.fct.2020.111816

Bombo, A.B., Pereira, A.E.S., Lusa, M.G., de Medeiros Oliveira, E., de Oliveira, J.L., Campos, E.V.R., de Jesus, M.B., Oliveira, H.C., Fraceto, L.F., Mayer, J.L.S., 2019. A mechanistic view of interactions of a nanoherbicide with target organism. J. Agric. Food Chem. 67, 4453–4462. https://doi.org/10.1021/acs.jafc.9b00806

Boyandin, A.A.-O., Kazantseva, E.A., 2021. Constructing slow-release formulations of herbicide metribuzin using its co-extrusion with biodegradable polyester poly-ε-caprolactone. J. Environ. Sci. Health.

Cabrera, A., Celis, R., Hermosín, M.C., 2016. Imazamox–clay complexes with chitosan- and iron(III)-modified smectites and their use in nanoformulations. Pest Manag. Sci. 72, 1285–1294. https://doi.org/10.1002/ps.4106

Cao, L., Zhou, Z., Niu, S., Cao, C., Li, X., Shan, Y., Huang, Q., 2018. Positive-charge functionalized mesoporous silica nanoparticles as nanocarriers for controlled 2,4-dichlorophenoxy acetic acid sodium salt release. J. Agric. Food Chem. 66, 6594–6603. https://doi.org/10.1021/acs.jafc.7b01957

Cartwright, A., Jackson, K., Morgan, C., Anderson, A., Britt, D.W., 2020. A review of metal and metal-oxide nanoparticle coating technologies to inhibit agglomeration and increase bioactivity for agricultural applications. Agronomy 10. https://doi.org/10.3390/agronomy10071018

Chen, C., Zhang, G., Dai, Z., Xiang, Y., Liu, B., Bian, P., Zheng, K., Wu, Z., Cai, D., 2018a. Fabrication of light-responsively controlled-release herbicide using a nanocomposite. Chem. Eng. J. 349, 101–110. https://doi.org/10.1016/j.cej.2018.05.079

Chen, X.-t, Wang, T., 2019. Preparation and characterization of atrazine-loaded biodegradable PLGA nanospheres. J. Integr. Agric. 18, 1035–1041. https://doi.org/10.1016/S2095-3119(19)62613-4

Chevillard, A., Angellier-Coussy, H., Guillard, V., Bertrand, C., Gontard, N., Gastaldi, E., 2014. Biodegradable herbicide delivery systems with slow diffusion in soil and UV protection properties. Pest Manag. Sci. 70, 1697–1705. https://doi.org/10.1002/ps.3705

Chevillard, A., Angellier-Coussy, H., Guillard, V., Gontard, N., Gastaldi, E., 2012. Investigating the biodegradation pattern of an ecofriendly pesticide delivery system based on wheat gluten and organically modified montmorillonites. Polym. Degrad. Stab. 97, 2060–2068. https://doi.org/10.1016/j.polymdegradstab.2012.02.017

Chi, Y., Chen, C., Zhang, G., Ye, Z., Su, X., Ren, X., Wu, Z., 2021. Fabrication of magnetic-responsive controlled-release herbicide by a palygorskite-based nanocomposite. Colloids Surf. B: Biointerfaces 208, 112115. https://doi.org/10.1016/j.colsurfb.2021.112115

Chi, Y., Zhang, G., Xiang, Y., Cai, D., Wu, Z., 2017. Fabrication of a temperature-controlled-release herbicide using a nanocomposite. ACS Sustain. Chem. Eng. 5, 4969–4975. https://doi.org/10.1021/acssuschemeng.7b00348

Clemente, Z., Grillo, R., Jonsson, M., Santos, N.Z.P., Feitosa, L.O., Lima, R., Fraceto, L.F., 2014. Ecotoxicological Eval. poly(Epsil. -caprolactone) nanocapsules Contain. triazine Herbic.

de Oliveira, C.R., Fraceto, L.F., Rizzi, G.M., Salla, R.F., Abdalla, F.C., Costa, M.J., Silva-Zacarin, E.C., 2016. Hepatic effects of the clomazone herbicide in both its free form and associated with chitosan-alginate nanoparticles in bullfrog tadpoles.

de Oliveira, J.L., Campos Ev Fau, -, Gonçalves da Silva, C.M., Gonçalves da Silva Cm Fau, -, Pasquoto, T., Pasquoto, T., Fau, -, Lima, R., Lima, R., Fau, -, Fraceto, L.F., Fraceto, L.F., 2015. Solid lipid nanoparticles co-loaded with simazine and atrazine: preparation, characterization, and evaluation of herbicidal activity. J. Agric. Food Chem.

de Oliveira, J.L., Campos, E.V.R., Pereira, A.E.S., Pasquoto, T., Lima, R., Grillo, R., Andrade, D.Jd, Santos, F.Ad, Fraceto, L.F., 2018. Zein nanoparticles as eco-friendly carrier systems for botanical repellents aiming sustainable agriculture. J. Agric. Food Chem. 66, 1330–1340. https://doi.org/10.1021/acs.jafc.7b05552

Demasi, S., Caser, M., Caldera, F., Dhakar, N.K., Vidotto, F., Trotta, F., Scariot, V., 2021. Functionalized dextrin-based nanosponges as effective carriers for the herbicide ailanthone. Ind. Crop. Prod. 164, 113346. https://doi.org/10.1016/j.indcrop.2021.113346

Deng, X., Zhao, P., Zhou, X., Bai, L., 2021. Excellent sustained-release efficacy of herbicide quinclorac with cationic covalent organic frameworks. Chem. Eng. J. 405, 126979. https://doi.org/10.1016/j.cej.2020.126979

Ding, K., Shi, L., Zhang, L., Zeng, T., Yin, Y., Yi, Y., 2016. Synthesis of photoresponsive polymeric propesticide micelles based on PEG for the controlled release of a herbicide. Polym. Chem. 7, 899–904. https://doi.org/10.1039/C5PY01690H

Diyanat, M., Saeidian, H., 2019. The metribuzin herbicide in polycaprolactone nanocapsules shows less plant chromosome aberration than non-encapsulated metribuzin.

Environ. Chem. Lett. 17, 1881–1888. https://doi.org/10.1007/s10311-019-00912-x
Diyanat, M., Saeidian, H., Baziar, S., Mirjafary, Z., 2019. Preparation and characterization of polycaprolactone nanocapsules containing pretilachlor as a herbicide nanocarrier. Environ. Sci. Pollut. Res. 26, 21579–21588. https://doi.org/10.1007/s11356-019-05257-0
Dong, J., Chen, W., Qin, D., Chen, Y., Li, J., Wang, C., Yu, Y., Feng, J., Du, X., 2021a. Cyclodextrin polymer-valved MoS2-embedded mesoporous silica nanopesticides toward hierarchical targets via multidimensional stimuli of biological and natural environments. J. Hazard. Mater. 419, 126404. https://doi.org/10.1016/j.jhazmat.2021.126404
Dong, J., Liu, X., Chen, Y., Yang, W., Du, X., 2021b. User-safe and efficient chitosan-gated porous carbon nanopesticides and nanoherbicides. J. Colloid Interface Sci. 594, 20–34. https://doi.org/10.1016/j.jcis.2021.03.001
FAO. The future of food and agriculture – Trends and challenges. Food and Agriculture Organization of the United Nations. 2017. 〈http://www.fao.org/3/a-i6583e.pdf〉.
Feng, S., Wang, J., Zhang, L., Chen, Q., Yue, W., Ke, N., Xie, H., 2020. Coumarin-Containing Light-Responsive Carboxymethyl Chitosan Micelles as Nanocarriers for Controlled Release of Pesticide. LID - 10.3390/polym12102268 [doi] LID - 2268. Polymers.
FAO, 2018. The future of food and agriculture – Alternative pathways to 2050. Food and Agriculture Organization of the United Nations, Rome, pp. 224.
Forini, M.M.L., Antunes, D.R., Cavalcante, L.A.F., Pontes, M.S., Biscalchim, É.R., Sanches, A.O., Santiago, E.F., Fraceto, L.F., Grillo, R., 2020. Fabrication and characterization of a novel herbicide delivery system with magnetic collectability and its phytotoxic effect on photosystem II of aquatic macrophyte. J. Agric. Food Chem. 68, 11105–11113. https://doi.org/10.1021/acs.jafc.0c03645
Fraceto, L.F., Grillo, R., de Medeiros, G.A., Scognamiglio, V., Rea, G., Bartolucci, C., 2016. Nanotechnology in agriculture: which innovation potential does it have. Front. Environ. Sci. 20. https://doi.org/10.3389/fenvs.2016.00020
Galán-Jiménez, M., Maria del Carmen E., Morillo, Bonnemoy, F., Mallet, C., Undabeytia, T., 2020. A sepiolite-based formulation for slow release of the herbicide mesotrione. Appl. Clay Sci. 189, 105503. https://doi.org/10.1016/j.clay.2020.105503
Gao, Y., Xiao, Y., Mao, K., Qin, X., Zhang, Y., Li, D., Zhang, Y., Li, J., Wan, H., He, S., 2020. Thermoresponsive polymer-encapsulated hollow mesoporous silica nanoparticles and their application in insecticide delivery. Chem. Eng. J. 383, 123169. https://doi.org/10.1016/j.cej.2019.123169
Gao, Y., Zhou, Z., Chen, X., Tian, Y., Li, Y., Wang, H., Li, X., Yu, X., 2021. Controlled release of herbicides by 2,4-D-, MCPA-, and bromoxynil-intercalated hydrotalcite nanosheets. Green Chem. 23. https://doi.org/10.1039/D1GC01349A
Ghaderpoori, M., Jafari, A.A.-O., Nazari, E., Rashidipour, M., Nazari, A., Chehelcheraghi, F., Kamarehie, B., Rezaee, R., 2020. Preparation and characterization of loaded paraquat- polymeric chitosan/xantan/tripolyphosphate nanocapsules and evaluation for controlled release. J. Environ. Health Sci. Eng.
Ghazali, S.A.I.S.M., Fatimah, I., Bohari, F.L., 2021a. Synthesis of hybrid organic-inorganic hydrotalcite-like materials intercalated with duplex herbicides: the characterization and simultaneous release properties. Molecules 26, 5086. https://doi.org/10.3390/molecules26165086
Ghazali, S.A.I.S.M., Hussein, M.Z., Subhan, R.H.Y., Sarijo, S.H., 2014. Formation of zinc-aluminium layered double hydroxide-2,4,5-tricholorophenoxybutyrate nanocomposites by ion exchange method. Adv. Mater. Res. 832, 374–378. https://doi.org/10.4028/www.scientific.net/AMR.832.374
Ghazali, S.A.I.S.M., Sarijo, S.H., Hussein, M.Z., 2021b. New synthesis of binate herbicide-interleaved anionic clay material: synthesis, characterization and simultaneous controlled-release properties. J. Porous Mater. 28, 495–505. https://doi.org/10.1007/s10934-020-01011-x
Giroto, A.S., de Campos, A., Pereira, E.I., Cruz, C.C.T., Marconcini, J.M., Ribeiro, C., 2014. Study of a nanocomposite starch–clay for slow-release of herbicides: Evidence of synergistic effects between the biodegradable matrix and exfoliated clay on herbicide release control. J. Appl. Polym. Sci. 131. https://doi.org/10.1002/app.41188
Gomes, S.I.L., Campos, E.V.R., Fraceto, L.F., Grillo, R., Scott-Fordsmand, J.J., Amorim, M.J.B., 2022. High-throughput transcriptomics reveals the mechanisms of nanopesticides – nanoformulation, commercial formulation, active ingredient – finding safe and sustainable-by-design (SSbD) options for the environment. Environ. Sci.: Nano. https://doi.org/10.1039/D1EN00735A
Gomollón-Bel, F., 2019. Ten chemical innovations that will change our world: IUPAC identifies emerging technologies in chemistry with potential to make our planet more sustainable. Chem. Int. 41, 12–17. https://doi.org/10.1515/ci-2019-0203
Granetto, M., Serpella, L., Fogliatto, S., Re, L., Bianco, C., Vidotto, F., Tosco, T., 2022. Natural clay and biopolymer-based nanopesticides to control the environmental spread of a soluble herbicide. Sci. Total Environ. 806, 151199. https://doi.org/10.1016/j.scitotenv.2021.151199
Grillo, R., Clemente, Z., Oliveira, J.Ld, Campos, E.V.R., Chalupe, V.C., Jonsson, C.M., Lima, Rd, Sanches, G., Nishisaka, C.S., Rosa, A.H., Oehlke, K., Greiner, R., Fraceto, L.F., 2015. Chitosan nanoparticles loaded the herbicide paraquat: the influence of the aquatic humic substances on the colloidal stability and toxicity. J. Hazard. Mater. 286, 562–572. https://doi.org/10.1016/j.jhazmat.2014.12.021
Grillo, R., dos Santos, N.Z.P., Maruyama, C.R., Rosa, A.H., de Lima, R., Fraceto, L.F., 2012. Poly(ε-caprolactone)nanocapsules as carrier systems for herbicides: Physico-chemical characterization and genotoxicity evaluation. J. Hazard. Mater. 231–232, 1–9. https://doi.org/10.1016/j.jhazmat.2012.06.019
Grillo, R., Fraceto, L.F., Amorim, M.J.B., Scott-Fordsmand, J.J., Schoonjans, R., Chaudhry, Q., 2021a. Ecotoxicological and regulatory aspects of environmental sustainability of nanopesticides. J. Hazard. Mater. 404, 124148. https://doi.org/10.1016/j.jhazmat.2020.124148
Grillo, R., Gallo, J., Stroppa, D.G., Carbó-Argibay, E., Lima, R., Fraceto, L.F., Bañobre-López, M., 2016. Sub-Micrometer Magnetic Nanocomposites: Insights into the Effect of Magnetic Nanoparticles Interactions on the Optimization of SAR and MRI Performance. Appl. Mater. Interfaces 8 (39), 25777–25787. https://doi.org/10.1021/acsami.6b08663
Grillo, R., Mattos, B.D., Antunes, D.R., Forini, M.M.L., Monikh, F.A., Rojas, O.J., 2021b. Foliage adhesion and interactions with particulate delivery systems for plant nanobionics and intelligent agriculture. Nano Today 37, 101078. https://doi.org/10.1016/j.nantod.2021.101078
Grillo, R., Pereira, A.E.S., Nishisaka, C.S., de Lima, R., Oehlke, K., Greiner, R., Fraceto, L.F., 2014. Chitosan/tripolyphosphate nanoparticles loaded with paraquat herbicide: An environmentally safer alternative for weed control. J. Hazard. Mater. 278, 163–171. https://doi.org/10.1016/j.jhazmat.2014.05.079
Grillo, R., Abhilash, P.C., Fraceto, L.F., 2016. Nanotechnology applied to bio-encapsulation of pesticides. J. Nanosci. Nanotechnol. 16 (1), 1231–1234. https://doi.org/10.1166/jnn.2016.12332
Guo, Y., Yang, Q., Yan, W., Li, B., Qian, K., Li, T., Xiao, W., He, L., 2014a. Controlled release of acetochlor from poly (butyl methacrylate-diacetone acrylamide) based formulation prepared by nanoemulsion polymerisation method and evaluation of the efficacy. Int. J. Environ. Anal. Chem. 94, 1001–1012.
Guo, Y., Yang, Q., Yan, W., Li, B., Qian, K., Li, T., Xiao, W., He, L., 2014b. Controlled release of acetochlor from poly (butyl methacrylate-diacetone acrylamide) based formulation prepared by nanoemulsion polymerisation method and evaluation of the efficacy. 1001-1012-2014 v.1094 no.1010. Int. J. Environ. Anal. Chem. https://doi.org/10.1080/03067319.2014.930844
Hao, L., Gong, L., Chen, L., Guan, M., Zhou, H., Qiu, S., Wen, H., Chen, H., Zhou, X., Akbulut, M., 2020a. Composite pesticide nanocarriers involving functionalized boron nitride nanoplatelets for pH-responsive release and enhanced UV stability. Chem. Eng. J. 396, 125233. https://doi.org/10.1016/j.cej.2020.125233
Hao, L., Lin, G., Lian, J., Chen, L., Zhou, H., Chen, H., Xu, H., Zhou, X., 2020b. Carboxymethyl cellulose capsulated zein as pesticide nano-delivery system for improving adhesion and anti-UV properties. Carbohydr. Polym. 231, 115725. https://doi.org/10.1016/j.carbpol.2019.115725
Hashim, N., Misuan, N.S., Isa, I.M., Bakar, S.A., Mustafar, S., Mamat, M., Hussein, M.Z., Sharif, S.N.M., 2020. Carboxymethylcellulose-coated magnesium-layered hydroxide nanocomposite for controlled release of 3-(4-methoxyphenyl)propionic acid. Arab. J. Chem. 13, 3974–3987. https://doi.org/10.1016/j.arabjc.2019.04.004
Hazrati, H., Saharkhiz, M.J., Niakousari, M., Moein, M., 2017. Natural herbicide activity of Satureja hortensis L. essential oil nanoemulsion on the seed germination and morphophysiological features of two important weed species. Ecotoxicol. Environ. Saf.
Heydari, M., Yousefi, A.R., Nikfarjam, N., Rahdar, A., Kyzas, G.Z., Bilal, M., 2021a. Plant-based nanoparticles prepared from protein containing tribenuron-methyl: fabrication, characterization, and application. Chem. Biol. Technol. Agric. 8, 53. https://doi.org/10.1186/s40538-021-00254-3
Heydari, M., Yousefi, A.R., Rahdar, A., Nikfarjam, N., Jamshidi, K., Bilal, M., Taboada, P., 2021b. Microemulsions of tribenuron-methyl using Pluronic F127: Physico-chemical characterization and efficiency on wheat weed. J. Mol. Liq. 326, 115263. https://doi.org/10.1016/j.molliq.2020.115263
Hofmann, T., Lowry, G.V., Ghoshal, S., Tufenkji, N., Brambilla, D., Dutcher, J.R., Gilbertson, L.M., Giraldo, J.P., Kinsella, J.M., Landry, M.P., Lovell, W., Naccache, R., Paret, M., Pedersen, J.A., Unrine, J.M., White, J.C., Wilkinson, K.J., 2020. Technology readiness and overcoming barriers to sustainably implement nanotechnology-enabled plant agriculture. Nat. Food 1 (7), 416–425.
Huang, S.A.-O.X., Van Aken, O.A.-O.X., Schwarzländer, M.A.-O., Belt, K.A.-O., Millar, A.H., 2016. The roles of mitochondrial reactive oxygen species in cellular signaling and stress response in plants. Plant Physiol.
Hussein, M., Hashim, N., Yahaya, A., Zainal, Z., 2010. Synthesis of an herbicides–inorganic nanohybrid compound by ion exchange-intercalation of 3(2-chlorophenoxy) propionate into layered double hydroxide. J. Exp. Nanosci. 5, 548–558. https://doi.org/10.1080/17458081003720639
Hussein, M., Nazarudin, N., Yarmo, A., 2012a. Synthesis of a layered organic-inorganic nanohybrid of 4-chlorophenoxyacetate-zinc-layered hydroxide with sustained release properties. J. Nanomater. 2012. https://doi.org/10.1155/2012/860352
Hussein, M.Z., Rahman, N.S.S.A., Sarijo, S.H., Zainal, Z., 2012b. Herbicide-intercalated zinc layered hydroxide nanohybrid for a dual-guest controlled release formulation. Int. J. Mol. Sci. 13, 7328–7342. https://doi.org/10.3390/ijms13067328
Hussein, M.Zb, Yahaya, A.H., Zainal, Z., Kian, L.H., 2005. Nanocomposite-based controlled release formulation of an herbicide, 2,4-dichlorophenoxyacetate incapsulated in zinc–aluminium-layered double hydroxide. Sci. Technol. Adv. Mater. 6, 956–962. https://doi.org/10.1016/j.stam.2005.09.004
Jacques, M.T., Oliveira, J.L., Campos, E.V., Fraceto, L.F., Ávila, D.S., 2017. Safety assessment of nanopesticides using the roundworm Caenorhabditis elegans.
Jambunathan, N., 2010. Determination and detection of reactive oxygen species (ROS), lipid peroxidation, and electrolyte leakage in plants. In: Sunkar, R. (Ed.), Plant Stress Tolerance: Methods and Protocols. Humana Press, Totowa, NJ, pp. 291–297. https://doi.org/10.1007/978-1-60761-702-0_18
Jiang, L.C., Basri, M., Omar, D., Rahman, M.B.A., Salleh, A.B., Rahman, R.N.Z.R.A., Selamat, A., 2012. Green nano-emulsion intervention for water-soluble glyphosate isopropylamine (IPA) formulations in controlling Eleusine indica (E. indica). Pestic. Biochem. Physiol. 102, 19–29. https://doi.org/10.1016/j.pestbp.2011.10.004
Jiang, Y., Chen, Y., Tian, D., Shen, F., Wan, X., Xu, L., Chen, Y., Zhang, H., Hu, J., Shen, F., 2020. Fabrication and characterization of lignin–xylan hybrid nanospheres as pesticide carriers with enzyme-mediated release property. Soft Matter 16, 9083–9093. https://doi.org/10.1039/D0SM01402H
Jubri, Zb, Yusoff, N.Z.Ab.M., Sarijo, S.Hb, Marsom, E.Sb, Hussein, M.Zb, 2017. Synthesis, characterization and controlled release properties of zinc–aluminium-beta-naphthoxyacetate nanocomposite. J. Porous Mater. 24, 573–582. https://doi.org/10.1007/s10934-016-0293-x

Kah, M., Tufenkji, N., White, J.C., 2019. Nano-enabled strategies to enhance crop nutrition and protection. Nat. Nanotechnol. 14 (6), 532–540. https://doi.org/10.1038/s41565-019-0439-5
Kah, M., Kookana, R.S., Gogos, A., Bucheli, T.D., 2018. A critical evaluation of nanopesticides and nanofertilizers against their conventional analogues. Nat. Nanotechnol. 13, 677–684. https://doi.org/10.1038/s41565-018-0131-1
Kah, M., Machinski P Fau - Koerner, P., Koerner P Fau - Tiede, K., Tiede K Fau - Grillo, R., Grillo R Fau - Fraceto, L.F., Fraceto Lf Fau - Hofmann, T., Hofmann, T., 2014. Analysing the fate of nanopesticides in soil and the applicability of regulatory protocols using a polymer-based nanoformulation of atrazine.
Kamari, A., Yusoff, S., 2019. N-octyl chitosan derivatives as amphiphilic carrier agents for herbicide formulations. Open Chem. 17, 365–380. https://doi.org/10.1515/chem-2019-0043
Kaur, P., Gupta, S., Kaur, K., Kaur, N., Kumar, R., Bhullar, M.S., 2021. Nanoemulsion of Foeniculum vulgare essential oil: a propitious striver against weeds of Triticum aestivum. Ind. Crop. Prod. 168, 113601. https://doi.org/10.1016/j.indcrop.2021.113601
Ke, M., Qu, Q., Peijnenburg, W.J.G.M., Li, X., Zhang, M., Zhang, Z., Lu, T., Pan, X., Qian, H., 2018. Phytotoxic effects of silver nanoparticles and silver ions to Arabidopsis thaliana as revealed by analysis of molecular responses and of metabolic pathways. Sci. Total Environ. 644, 1070–1079. https://doi.org/10.1016/j.scitotenv.2018.07.061
Ke, M., Ye, Y., Zhang, Z., Gillings, M., Qu, Q., Xu, N., Xu, L., Lu, T., Wang, J., Qian, H., 2021. Synergistic effects of glyphosate and multiwall carbon nanotubes on Arabidopsis thaliana physiology and metabolism. Sci. Total Environ. 769, 145156. https://doi.org/10.1016/j.scitotenv.2021.145156
Khatem, R., Celis, R., Hermosín, M.C., 2019. Cationic and anionic clay nanoformulations of imazamox for minimizing environmental risk. Appl. Clay Sci. 168, 106–115. https://doi.org/10.1016/j.clay.2018.10.014
Kumar, A., Choudhary, A., Kaur, H., Mehta, S.A.-O., Husen, A.A.-O., 2021. Smart nanomaterial and nanocomposite with advanced agrochemical activities.https://doi.org/https://doi.org/10.1186/s11671–021-03612–0.
Kumar, N., Kumar, R., Shakil, N., Das, T., 2016. Nanoformulations of pretilachlor herbicide: preparation, characterization and activity. J. Sci. Ind. Res. 75, 676–680.
Kumar, S., Bhanjana, G., Sharma, A., Dilbaghi, N., Sidhu, M.C., Kim, K.-H., 2017a. Development of nanoformulation approaches for the control of weeds. Sci. Total Environ. 586, 1272–1278. https://doi.org/10.1016/j.scitotenv.2017.02.138
Kumar, S., Bhanjana, G., Sharma, A., Sarita, Sidhu, M., Dilbaghi, N., 2014. Herbicide loaded carboxymethyl cellulose nanocapsules as potential carrier in agrinanotechnology. Sci. Adv. Mater. 7. https://doi.org/10.1166/sam.2015.2243
Kumar, V., Singh, A., Das, T.K., Sarkar, D.J., Singh, S.B., Dhaka, R., Kumar, A., 2017b. Release behavior and bioefficacy of imazethapyr formulations based on biopolymeric hydrogels.
Larue, C., Castillo-Michel, H., Sobanska, S., Trcera, N., Sorieul, S., Cécillon, L., Ouerdane, L., Legros, S., Sarret, G., 2014. Fate of pristine TiO_2 nanoparticles and aged paint-containing TiO_2 nanoparticles in lettuce crop after foliar exposure. J. Hazard. Mater. 273, 17–26. https://doi.org/10.1016/j.jhazmat.2014.03.014
Lee, S., Wang, G., Ji, N., Zhang, M., Wang, D., Sun, L., Meng, W., Zheng, Y., Li, Y., Wu, Y., 2022. Synthesis, characterizations and kinetics of MOF-5 as herbicide vehicle and its controlled release in PVA/ST biodegradable composite membranes. Z. für Anorg. und Allg. Chem. 648, e202100252. https://doi.org/10.1002/zaac.202100252
Li, P., Huang, Y., Fu, C., Jiang, S.X., Peng, W., Jia, Y., Peng, H., Zhang, P., Manzie, N., Mitter, N., Xu, Z.P., 2021. Eco-friendly biomolecule-nanomaterial hybrids as next-generation agrochemicals for topical delivery. EcoMat 3, e12132. https://doi.org/10.1002/eom2.12132
Liang, J., Yu, M., Guo, L., Cui, B., Zhao, X., Sun, C., Wang, Y., Liu, G., Cui, H., Zeng, Z., 2018. Bioinspired development of P(St–MAA)–avermectin nanoparticles with high affinity for foliage to enhance folia retention. J. Agric. Food Chem. 66, 6578–6584. https://doi.org/10.1021/acs.jafc.7b01998
Lim, C.J., Basri M Fau - Omar, D., Omar D Fau - Abdul Rahman, M.B., Abdul Rahman Mb Fau - Salleh, A.B., Salleh Ab Fau - Raja Abdul Rahman, R.N.Z., Raja Abdul Rahman, R.N., 2013a. Green nanoemulsion-laden glyphosate isopropylamine formulation in suppressing creeping foxglove (A. gangetica), slender button weed (D. ocimifolia) and buffalo grass (P. conjugatum). Pest Manag. Sci.
Lim, C.J., Basri M Fau - Omar, D., Omar D Fau - Abdul Rahman, M.B., Abdul Rahman Mb Fau - Salleh, A.B., Salleh Ab Fau - Raja Abdul Rahman, R.N.Z., Raja Abdul Rahman, R. N., 2013b. Green nanoemulsion-laden glyphosate isopropylamine formulation in suppressing creeping foxglove (A. gangetica), slender button weed (D. ocimifolia) and buffalo grass (P. conjugatum).
Lim, C.J., Basri, M., Omar, D., Abdul Rahman, M.B., Salleh, A.B., Raja Abdul Rahman, R.N.Z., 2012. Physicochemical characterization and formation of glyphosate-laden nano-emulsion for herbicide formulation. Ind. Crop. Prod. 36, 607–613. https://doi.org/10.1016/j.indcrop.2011.11.005
Lim, G.-H., Liu, H., Yu, K., Liu, R., Shine, M.B., Fernandez, J., Burch-Smith, T., Mobley Justin, K., McLetchie, N., Kachroo, A., Kachroo, P., 2020. The plant cuticle regulates apoplastic transport of salicylic acid during systemic acquired resistance. Sci. Adv. https://doi.org/10.1126/sciadv.aaz0478
Lima, P.H.Cd, Antunes, D.R., Forini, M.Md.L., Pontes, Md.S., Mattos, B.D., Grillo, R., 2021. Recent advances on lignocellulosic-based nanopesticides for agricultural applications. Front. Nanotechnol. 3.
Lima, P.H.C., Tavares, A.A., de Lima Silva, S.M., de Moura, M.R., Aouada, F.A., Grillo, R., 2022. Recent advances on nanohybrid systems constituting clay–chitosan with organic molecules–a review. Appl. Clay Sci. 226, 106548.
Liu, B., Chen, C., Wang, R., Dong, S., Li, J., Zhang, G., Cai, D., Zhai, S., Wu, Z., 2019. Near-infrared light-responsively controlled-release herbicide using biochar as a photothermal agent. ACS Sustain. Chem. Eng. 7, 14924–14932. https://doi.org/10.1021/acssuschemeng.9b03123
Liu, C., Wang, A., Yin, H., Shen, Y., Jiang, T., 2012. Preparation of nanosized hollow silica spheres from Na2SiO3 using Fe3O4 nanoparticles as templates. Particuology 10, 352–358. https://doi.org/10.1016/j.partic.2011.04.009
López-Cabeza, R., Poiger, T., Cornejo, J., Celis, R.A.-O., 2019. A clay-based formulation of the herbicide imazaquin containing exclusively the biologically active enantiomer.
Machado, T.O., Grabow, J., Sayer, C., de Araújo, P.H.H., Ehrenhard, M.L., Wurm, F.R., 2022. Biopolymer-based nanocarriers for sustained release of agrochemicals: a review on materials and social science perspectives for a sustainable future of agri- and horticulture. Adv. Colloid Interface Sci. 303, 102645. https://doi.org/10.1016/j.cis.2022.102645
Maes, C.A.-O.X., Brostaux, Y.A.-O., Bouquillon, S., Fauconnier, M.A.-O., 2021. Use of New Glycerol-Based Dendrimers for Essential Oils Encapsulation: Optimization of Stirring Time and Rate Using a Plackett-Burman Design and a Surface Response Methodology. LID - 10.3390/foods10020207 [doi] LID - 207.
Mahajan, R.A.-O., Selim, A.A.-O.X., Neethu, K.A.-O., Sharma, S.A.-O., Shanmugam, V.A.-O., Jayamurugan, G.A.-O., 2021. A systematic study to unravel the potential of using polysaccharides based organic-nanoparticles versus hybrid-nanoparticles for pesticide delivery. LID - 10.1088/1361–6528/ac1bdc [doi]. Nanotechnology.
Mahmoudian, M., Torbati, S., AliMirzayi, N., Nozad, E., Kochameshki, M.G., Shokri, A., 2020. Preparation and investigation of poly(methylmethacrylate) nano-capsules containing haloxyfop-R-methyl and their release behavior. J. Environ. Sci. Health.
Manke, A., Wang, L., Fau, -, Rojanasakul, Y., Rojanasakul, Y., 2013. Mechanisms of nanoparticle-induced oxidative stress and toxicity. BioMed. Res. Int.
Marco-Brown, J.L., Barbosa-Lema, C.M., Torres Sánchez, R.M., Mercader, R.C., dos Santos Afonso, M., 2012. Adsorption of picloram herbicide on iron oxide pillared montmorillonite. Appl. Clay Sci. 58, 25–33. https://doi.org/10.1016/j.clay.2012.01.004
Marco-Brown, J.L., Undabeytia, T., Torres Sánchez, R.M., Dos Santos Afonso, M., 2017. Slow-release formulations of the herbicide picloram by using Fe-Al pillared montmorillonite. Environ. Sci. Pollut. Res.
Maruyama, C.R., Guilger, M., Pascoli, M., Bileshy-José, N., Abhilash, P.C., Fraceto, L.F., de Lima, R., 2016. Nanoparticles Based on Chitosan as Carriers for the Combined Herbicides Imazapic and Imazapyr. Sci. Rep. 6, 19768. https://doi.org/10.1038/srep19768
Mattos, B.D., Tardy, B.L., Magalhães, W.L.E., Rojas, O.J., 2017. Controlled release for crop and wood protection: Recent progress toward sustainable and safe nanostructured biocidal systems. J. Control. Release 262, 139–150. https://doi.org/10.1016/j.jconrel.2017.07.025
Mejías, F.J.R., Trasobares, S., Varela, R.M., Molinillo, J.M.G., Calvino, J.J., Macías, F.A., 2021. One-step encapsulation of ortho-disulfides in functionalized zinc MOF. Enabling Metal–Organic Frameworks in Agriculture. ACS Appl. Mater. Interfaces 13, 7997–8005. https://doi.org/10.1021/acsami.0c21488
Mittal, D., Kaur, G., Singh, P., Yadav, K., Ali, S.A., 2020. Nanoparticle-based sustainable agriculture and food science: recent advances and future outlook. Front. Nanotechnol. 2.
Mohammadi, Z., Eini, M., Rastegari, A., Tehrani, M.R., 2021. Chitosan as a machine for biomolecule delivery: a review. Carbohydr. Polym. 256, 117414. https://doi.org/10.1016/j.carbpol.2020.117414
Moore, A.J.S., Dean, L.S.N., Yam, A.N.K., de Lima, R., Fraceto, L.F., Tetley, T.D., 2022. Bioreactivity of a novel poly(epsilon-caprolactone) nanocapsule containing atrazine with human lung alveolar epithelial cells. Environ. Sci.: Nano. https://doi.org/10.1039/D1EN01068A
Moreno, A., Jordana, A., Grillo, R., Fraceto, L., Jaime, C., 2018. A study on the molecular existing interactions in nanoherbicides: a chitooligosaccharide/tripolyphosphate loaded with paraquat case. Colloids Surf. A: Physicochem. Eng. Asp. 562. https://doi.org/10.1016/j.colsurfa.2018.11.033
Mujtaba, M., Khawar, K.M., Camara, M.C., Carvalho, L.B., Fraceto, L.F., Morsi, R.E., Elsabee, M.Z., Kaya, M., Labidi, J., Ullah, H., Wang, D., 2020. Chitosan-based delivery systems for plants: a brief overview of recent advances and future directions. Int. J. Biol. Macromol. 154, 683–697. https://doi.org/10.1016/j.ijbiomac.2020.03.128
Nadiminti, P.P., Rookes, J.E., Dong, Y.D., Sayer, C., Boyd, B.J., Cahill, D.M., 2016. Nanostructured liquid crystalline particle assisted delivery of 2,4-dichlorophenoxyacetic acid to weeds, crops and model plants. Crop Prot. 82, 17–29. https://doi.org/10.1016/j.cropro.2015.12.018
Nadiminti, P.P., Sharma, H., Kada, S.R., Pfeffer, F.M., O'Dell, L.A., Cahill, D.M., 2019. Use of Mg–Al nanoclay as an efficient vehicle for the delivery of the herbicide 2,4-dichlorophenoxyacetic acid. ACS Sustain. Chem. Eng. 7, 10962–10970. https://doi.org/10.1021/acssuschemeng.9b02001
Namasivayam, K.R.S., Aruna, A., Gokila, 2014. Evaluation of silver nanoparticles-chitosan encapsulated synthetic herbicide paraquat (AgNp-CS-PQ) preparation for the controlled release and improved herbicidal activity against Eichhornia crassipes. Res. J. Biotechnol. 9, 19–27.
Natarelli, C.V.L., Claro, P.I.C., Miranda, K.W.E., Ferreira, G.M.D., de Oliveira, J.E., Marconcini, J.M., 2019. 2,4-Dichlorophenoxyacetic acid adsorption on montmorillonite organoclay for controlled release applications. SN Appl. Sci. 1, 1212. https://doi.org/10.1007/s42452-019-1235-4
Okeke, E.S., Ezeorba, T.P.C., Mao, G., Chen, Y., Feng, W., Wu, X., 2021. Nano-enabled agrochemicals/materials: Potential human health impact, risk assessment, management strategies and future prospects (https:// doi.org/). Environ. Pollut., 118722. https://doi.org/10.1016/j.envpol.2021.118722
Oliveira-Pinto, P.R., Mariz-Ponte, N., Torres, A., Tavares, F., Fernandes-Ferreira, M., Sousa, R.M., Santos, C., 2022. Satureja montana L. essential oil, montmorillonite and nanoformulation reduce Xanthomonas euvesicatoria infection, modulating redox and hormonal pathways of tomato plants. Sci. Hortic. 295, 110861. https://doi.org/10.1016/j.scienta.2021.110861
Oliveira, H.C., Stolf-Moreira, R., Martinez, C.B., Grillo, R., de Jesus, M.B., Fraceto, L.F., 2015a. Nanoencapsulation enhances the post-emergence herbicidal activity of

atrazine against mustard plants. PLoS One 10, e0132971. https://doi.org/10.1371/journal.pone.0132971

Oliveira, H.C., Stolf-Moreira, R., Martinez, C.B.R., Sousa, G.F.M., Grillo, R., de Jesus, M.B., Fraceto, L.F., 2015b. Evaluation of the side effects of poly(epsilon-caprolactone) nanocapsules containing atrazine toward maize plants. Front. Chem. 3. https://doi.org/10.3389/fchem.2015.00061

Panariti, A., Miserocchi, G., Rivolta, I., 2012. The effect of nanoparticle uptake on cellular behavior: disrupting or enabling functions. Nanotechnol. Sci. Appl. 5, 87–100. https://doi.org/10.2147/NSA.S25515

Paulraj, G.M., Ignacimuthu, S., Rajiv, G.M., Shajahan, A., Ganesan, P., Packiam, S.M., Al-Dhabi, N.A., 2017. Comparative studies of Tripolyphosphate and Glutaraldehyde cross-linked chitosan-botanical pesticide nanoparticles and their agricultural applications. Int. J. Biol. Macromol. 104. https://doi.org/10.1016/j.ijbiomac.2017.06.043

Peixoto, S., Henriques, I., Loureiro, S., 2021. Long-term effects of Cu(OH)2 nanopesticide exposure on soil microbial communities. Environ. Pollut. 269, 116113. https://doi.org/10.1016/j.envpol.2020.116113

Pereira, A.E.S., Grillo, R., Mello, N.F.S., Rosa, A.H., Fraceto, L.F., 2014. Application of poly(epsilon-caprolactone) nanoparticles containing atrazine herbicide as an alternative technique to control weeds and reduce damage to the environment. J. Hazard. Mater. 268, 207–215. https://doi.org/10.1016/j.jhazmat.2014.01.025

Pereira, A.E.S., Narciso, A.M., Seabra, A.B., Fraceto, L.F., 2015. Evaluation of the effects of nitric oxide-releasing nanoparticles on plants. J. Phys.: Conf. Ser. 617, 012025. https://doi.org/10.1088/1742-6596/617/1/012025

Pérez-de-Luque, A., 2017. Interaction of Nanomaterials with Plant.: What Do We Need Real. Appl. Agric. ? Front. Environ. Sci. 5.

Petit, A.N., Debenest, T., Gagné, F., 2012. Dendrimers increase glyphosate formulation toxicity to Chlamydomonas reinhardtii. Fresenius Environ. Bull. 21, 1967–1971.

Pontes, M.S., Antunes, D.R., Oliveira, I.P., Forini, M.M.L., Santos, J.S., Arruda, G.J., Caires, A.R.L., Santiago, E.F., Grillo, R., 2021. Chitosan/tripolyphosphate nanoformulation carrying paraquat: insights on its enhanced herbicidal activity. Environ. Sci.: Nano 8, 1336–1351. https://doi.org/10.1039/D0EN01128B

Popp, J., Peto, K., Nagy, J., 2013. Pesticide productivity and food security. A review. Agron. Sustain. Dev. 33, 243–255. https://doi.org/10.1007/s13593-012-0105-x

Preisler, A.C., Pereira, A.E., Campos, E.V., Dalazen, G., Fraceto, L.A.-O., Oliveira, H.A.-O., 2020. Atrazine nanoencapsulation improves pre-emergence herbicidal activity against Bidens pilosa without enhancing long-term residual effect on Glycine max. Pest Manag. Sci.

Rashidipour, M., Maleki, A., Kordi, S., Birjandi, M., Pajouhi, N., Mohammadi, E., Heydari, R., Rezaee, R., Rasoulian, B., Davari, B., 2019. Pectin/chitosan/tripolyphosphate nanoparticles: efficient carriers for reducing soil sorption, cytotoxicity, and mutagenicity of paraquat and enhancing its herbicide activity. J. Agric. Food Chem. 67, 5736–5745. https://doi.org/10.1021/acs.jafc.9b01106

Rashidzadeh, A., Olad, A., Hejazi, M.J., 2017. Controlled release systems based on intercalated paraquat onto montmorillonite and clinoptilolite clays encapsulated with sodium alginate. Adv. Polym. Technol. 36, 177–185. https://doi.org/10.1002/adv.21597

Rastogi, A., Zivcak, M., Sytar, O., Kalaji, H.M., He, X., Mbarki, S., Brestic, M., 2017. Impact of metal and metal oxide nanoparticles on plant: a critical review. Front. Chem. 5. https://doi.org/10.3389/fchem.2017.00078

Rebitski, E.A.-O., Darder, M.A.-O., Aranda, P.A.-O., 2019. Layered double hydroxide/sepiolite hybrid nanoarchitectures for the controlled release of herbicides.

Reddy, S.S., & Chhabra, V. 2022. Nanotechnology: its scope in agriculture. Journal of Physics: Conference Series 2267,1, 012112).

Rojas, S., Rodríguez-Diéguez, A., Horcajada, P., 2022. Metal–organic frameworks in agriculture. ACS Appl. Mater. Interfaces 14, 16983–17007. https://doi.org/10.1021/acsami.2c00615

Rychter, P., 2019. Chitosan/glyphosate formulation as a potential, environmental friendly herbicide with prolonged activity. J. Environ. Sci. Health, Part B 54, 681–692. https://doi.org/10.1080/03601234.2019.1632644

Santana, I., Wu, H., Hu, P., Giraldo, J.P., 2020. Targeted delivery of nanomaterials with chemical cargoes in plants enabled by a biorecognition motif. Nat. Commun. 11 (2045), 2020. https://doi.org/10.1038/s41467-020-15731-w

Santiago, E.F., Pontes, M.S., Arruda, G.J., Caires, A.R.L., Colbeck, I., Maldonado-Rodriguez, R., Grillo, R., 2020. Understanding the interaction of nanopesticides with plants. In: Fraceto, L.F., de Castro, S.S., Grillo, V.L., Ávila, R., Caixeta Oliveira, D., Lima, R., H. (Eds.), Nanopesticides: From Research and Development to Mechanisms of Action and Sustainable Use in Agriculture. Springer International Publishing, Cham, pp. 69–109. https://doi.org/10.1007/978-3-030-44873-8_4

Sarkar, M.R., Rashid, M.H.O., Rahman, A., Kafi, M.A., Hosen, M.I., Rahman, M.S., Khan, M.N., 2022. Recent advances in nanomaterials based sustainable agriculture: an overview. Environ. Nanotechnol. Monit. Manag. 18, 100687. https://doi.org/10.1016/j.enmm.2022.100687

Sarijo, S.H., Ghazali, S.A.I.S.M., Hussein, M.Z., 2013. Synthesis of nanocomposite 2-methyl-4-chlorophenoxyacetic acid with layered double hydroxide: Physicochemical characterization and controlled release properties. J. Nanopart. Res. 15. https://doi.org/10.1007/s11051-012-1356-9

Sarijo, S.H., Ghazali, S.A.I.S.M., Hussein, M.Z., 2015. Synthesis of dual herbicides-intercalated hydrotalcite-like nanohybrid compound with simultaneous controlled release property. J. Porous Mater. 22, 473–480. https://doi.org/10.1007/s10934-015-9916-x

Schnoor, B., Elhendawy, A., Joseph, S., Putman, M., Chacón-Cerdas, R., Flores-Mora, D., Bravo-Moraga, F., Gonzalez-Nilo, F., Salvador-Morales, C., 2018. Engineering atrazine loaded poly (lactic-co-glycolic acid) nanoparticles to ameliorate environmental challenges. J. Agric. Food Chem. 66, 7889–7898. https://doi.org/10.1021/acs.jafc.8b01911

Schwab, F., Bucheli, T.D., Camenzuli, L., Magrez, A., Knauer, K., Sigg, L., Nowack, B., 2013. Diuron sorbed to carbon nanotubes exhibits enhanced toxicity to chlorella vulgaris. Environ. Sci. Technol. 47, 7012–7019. https://doi.org/10.1021/es304016u

Shakiba, S., Astete, C.E., Paudel, S., Sabliov, C.M., Rodrigues, D.F., Louie, S.M., 2020. Emerging investigator series: polymeric nanocarriers for agricultural applications: synthesis, characterization, and environmental and biological interactions. Environ. Sci.: Nano 7, 37–67. https://doi.org/10.1039/c9en01127g

Shan, Y., Cao, L., Xu, C., Zhao, P., Cao, C., Li, F., Xu, B., Huang, Q., 2019. Sulfonate-functionalized mesoporous silica nanoparticles as carriers for controlled herbicide diquat dibromide release through electrostatic interaction. Int J. Mol. Sci. 20, 1330. https://doi.org/10.3390/ijms20061330

Sharif, S.N.M., Hashim, N., Isa, I.M., Bakar, S.A., Saidin, M.I., Ahmad, M.S., Mamat, M., Hussein, M.Z., 2020a. Controlled release formulation of zinc hydroxide nitrate intercalated with sodium dodecylsulphate and bispyribac anions: A novel herbicide nanocomposite for paddy cultivation. Arab. J. Chem. 13, 4513–4527. https://doi.org/10.1016/j.arabjc.2019.09.006

Sharif, S.N.M., Hashim, N., Isa, I.M., Bakar, S.A., Saidin, M.I., Ahmad, M.S., Mamat, M., Hussein, M.Z., 2020b. The influence of chitosan coating on the controlled release behaviour of zinc/aluminium-layered double hydroxide-quinclorac composite. Mater. Chem. Phys. 251, 123076. https://doi.org/10.1016/j.matchemphys.2020.123076

Sharif, S.N.M., Hashim, N., Isa, I.M., Bakar, S.A., Saidin, M.I., Ahmad, M.S., Mamat, M., Hussein, M.Z., Zainul, R., 2021. Polymeric nanocomposite-based herbicide of carboxymethyl cellulose coated-zinc/aluminium layered double hydroxide-quinclorac: a controlled release purpose for agrochemicals. J. Polym. Environ. 29, 1817–1834. https://doi.org/10.1007/s10924-020-01997-0

Sharif, S.N.M., Hashim, N., md isa, I., Mamat, M., Mohd Ali, N., Suriani, A.B., Hussein, M., Mustafar, S., 2020c. The intercalation behaviour and physico-chemical characterisation of novel intercalated nanocomposite from zinc/aluminium layered double hydroxides and broadleaf herbicide clopyralid. Chem. Chem. Technol. 14, 38–46. https://doi.org/10.23939/chcht14.01.038

Sharma, A., Kumar, V., Shahzad, B., Tanveer, M., Sidhu, G.P.S., Handa, N., Kohli, S.K., Yadav, P., Bali, A.S., Parihar, R.D., Dar, O.I., Singh, K., Jasrotia, S., Bakshi, P., Ramakrishnan, M., Kumar, S., Bhardwaj, R., Thukral, A.K., 2019. Worldwide pesticide usage and its impacts on ecosystem. SN Appl. Sci. 1, 1446. https://doi.org/10.1007/s42452-019-1485-1

Shekhar, S., Sharma, S., Kumar, A., Taneja, A., Sharma, B., 2021. The framework of nanopesticides: a paradigm in biodiversity. Mater. Adv. 2, 6569–6588. https://doi.org/10.1039/D1MA00329A

Shen, Y., Borgatta, J., Ma, C., Singh, G., Tamez, C., Schultes, N.P., Zhang, Z., Dhankher, O.P., Elmer, W.H., He, L., Hamers, R.J., White, J.C., 2022. Role of foliar biointerface properties and nanomaterial chemistry in controlling cu transfer into wild-type and mutant arabidopsis thaliana leaf tissue. J. Agric. Food Chem. 70, 4267–4278. https://doi.org/10.1021/acs.jafc.1c07873

Shen, Z., Zhou, X., Sun, X., Xu, H., Chen, H., Zhou, H., 2019. Preparation of 2,4-dichlorophenoxyacetic acid loaded on cysteamine-modified polydopamine and its release behaviors. J. Appl. Polym. Sci. 136, 47469. https://doi.org/10.1002/app.47469

Silva, Md.S., Cocenza, D.S., Grillo, R., Melo, N.F.Sd, Tonello, P.S., Oliveira, L.Cd, Cassimiro, D.L., Rosa, A.H., Fraceto, L.F., 2011. Paraquat-loaded alginate/chitosan nanoparticles: preparation, characterization and soil sorption studies. J. Hazard. Mater. 190, 366–374. https://doi.org/10.1016/j.jhazmat.2011.03.057

Silva, Md.S., Cocenza, D.S., Rosa, A.H., Fraceto, L.F., 2012. Efeito da associação do herbicida clomazone a nanoesferas de alginato/quitosana na sorção em solos. Quím. Nova 35, 102–107.

Singh, A., Dhiman, N., Kar, A.K., Singh, D., Purohit, M.P., Ghosh, D., Patnaik, S., 2020. Advances in controlled release pesticide formulations: Prospects to safer integrated pest management and sustainable agriculture. J. Hazard. Mater. 385, 121525. https://doi.org/10.1016/j.jhazmat.2019.121525

Singh, N., Manshian, B., Jenkins, G.J.S., Griffiths, S.M., Williams, P.M., Maffeis, T.G.G., Wright, C.J., Doak, S.H., 2009. NanoGenotoxicology: The DNA damaging potential of engineered nanomaterials. Biomaterials 30, 3891–3914. https://doi.org/10.1016/j.biomaterials.2009.04.009

Sinisi, V., Pelagatti, P., Carcelli, M., Migliori, A., Mantovani, L., Righi, L., Leonardi, G., Pietarinen, S., Hubsch, C., Rogolino, D., 2019. A green approach to copper-containing pesticides: antimicrobial and antifungal activity of brochantite supported on lignin for the development of biobased plant protection products. ACS Sustain. Chem. Eng. 7, 3213–3221. https://doi.org/10.1021/acssuschemeng.8b05135

Song, S., Wang, Y., Xie, J., Sun, B., Zhou, N., Shen, H., Shen, J., 2019. Carboxymethyl chitosan modified carbon nanoparticle for controlled emamectin benzoate delivery: improved solubility, pH-responsive release, and sustainable pest control. ACS Appl. Mater. Interfaces 11, 34258–34267. https://doi.org/10.1021/acsami.9b12564

Sousa, G.F.M., Gomes, D.G., Campos, E.V.R., Oliveira, J.L., Fraceto, L.F., Stolf-Moreira, R., Oliveira, H.C., 2018. Post-emergence herbicidal activity of nanoatrazine against susceptible weeds. Front. Environ. Sci. 6. https://doi.org/10.3389/fenvs.2018.00012

Souza, P.M.S., Lobo, F.A., Rosa, A.H., Fraceto, L.F., 2012. Development of nanocapsules of poly-e-caprolactone containing herbicide atrazine. Quím. Nova.

Stępiński, D., Kwiatkowska, M., Wojtczak, A., Polit, J.T., Domínguez, E., Heredia, A., Popłońska, K., 2020. The role of cutinsomes in plant cuticle formation. Cells 9. https://doi.org/10.3390/cells9081778

Sun, H., Jiang, C., Wu, L., Bai, X., Zhai, S., 2019. Cytotoxicity-related bioeffects induced by nanoparticles: the role of surface chemistry. 414-414. Front. Bioeng. Biotechnol. 7. https://doi.org/10.3389/fbioe.2019.00414

Taban, A., Saharkhiz, M.J., Kavoosi, G., 2021. Development of pre-emergence herbicide based on arabic gum-gelatin, apple pectin and savory essential oil nano-particles: a potential green alternative to metribuzin. Int. J. Biol. Macromol. 167, 756–765. https://doi.org/10.1016/j.ijbiomac.2020.12.007

Taban, A., Saharkhiz, M.J., Khorram, M., 2020. Formulation and assessment of nano-encapsulated bioherbicides based on biopolymers and essential oil. Ind. Crop. Prod. 149, 112348. https://doi.org/10.1016/j.indcrop.2020.112348

Takeshita, V., de Sousa, B.T., Preisler, A.C., Carvalho, L.B., Pereira, Ad.E.S., Tornisielo, V.L., Dalazen, G., Oliveira, H.C., Fraceto, L.F., 2021. Foliar absorption and field herbicidal studies of atrazine-loaded polymeric nanoparticles. J. Hazard. Mater. 418, 126350. https://doi.org/10.1016/j.jhazmat.2021.126350
Tan, D., Yuan, P., Annabi-Bergaya, F., Dong, F., Liu, D., He, H., 2015a. A comparative study of tubular halloysite and platy kaolinite as carriers for the loading and release of the herbicide amitrole. Appl. Clay Sci. 114, 190–196. https://doi.org/10.1016/j.clay.2015.05.024
Tan, D., Yuan, P., Annabi-Bergaya, F., Liu, D., He, H., 2015b. Methoxy-modified kaolinite as a novel carrier for high-capacity loading and controlled-release of the herbicide amitrole. Sci. Rep. 5. https://doi.org/10.1038/srep08870
Tan, S., Wu, X., Xing, Y., Lilak, S., Wu, M., Zhao, J.X., 2020. Enhanced synergetic antibacterial activity by a reduce graphene oxide/Ag nanocomposite through the photothermal effect. Colloids Surf. B: Biointerfaces 185, 110616. https://doi.org/10.1016/j.colsurfb.2019.110616
Tong, Y., Wu, Y., Zhao, C., Xu, Y., Lu, J., Xiang, S., Zong, F., Wu, X., 2017. Polymeric nanoparticles as a metolachlor carrier: water-based formulation for hydrophobic pesticides and absorption by plants. J. Agric. Food Chem. 65, 7371–7378. https://doi.org/10.1021/acs.jafc.7b02197
Torbati, S., Mahmoudian, M., Alimirzaei, N., 2018. Nanocapsulation of herbicide Haloxyfop-R-methyl in poly(methyl methacrylate): phytotoxicological effects of pure herbicide and its nanocapsulated form on duckweed as a model macrophyte. Turk. J. Chem. 42. https://doi.org/10.3906/kim-1705-70
Touloupakis, E., Margelou, A., Ghanotakis, D., 2011. Intercalation of the herbicide atrazine in layered double hydroxides for controlled-release applications. Pest Manag. Sci. 67, 837–841. https://doi.org/10.1002/ps.2121
Tripathi, D.K., Shweta, Singh, S., Singh, S., Pandey, R., Singh, V.P., Sharma, N.C., Prasad, S.M., Dubey, N.K., Chauhan, D.K., 2017. An overview on manufactured nanoparticles in plants: Uptake, translocation, accumulation and phytotoxicity. Plant Physiol. Biochem. 110, 2–12. https://doi.org/10.1016/j.plaphy.2016.07.030
Walkey, C.D., Chan, W.C.W., 2012. Understanding and controlling the interaction of nanomaterials with proteins in a physiological environment. Chem. Soc. Rev. 41, 2780–2799. https://doi.org/10.1039/C1CS15233E
Wang, D., Saleh, N.B., Byro, A., Zepp, R., Sahle-Demessie, E., Luxton, T.P., Ho, K.T., Burgess, R.M., Flury, M., White, J.C., Su, C., 2022a. Nano-enabled pesticides for sustainable agriculture and global food security. Nat. Nanotechnol. 17, 347–360. https://doi.org/10.1038/s41565-022-01082-8
Wang, J., Xie, H., Han, J., Li, J., Lin, X., Wang, X., 2022b. Effect of graphene oxide-glyphosate nanocomposite on wheat and rape seedlings: growth, photosynthesis performance, and oxidative stress response. Environ. Technol. Innov. 27, 102527. https://doi.org/10.1016/j.eti.2022.102527
Wang, X., Qin, Y., Li, X., Yan, B.A.-O., Martyniuk, C.J., 2021. Comprehensive interrogation of metabolic and bioenergetic responses of early-staged zebrafish (Danio rerio) to a commercial copper hydroxide nanopesticide. Environ. Sci. Technol.
Wen, Y., Zhang, L., Chen, Z., Sheng, X., Qiu, J., Xu, D., 2016. Co-exposure of silver nanoparticles and chiral herbicide imazethapyr to Arabidopsis thaliana: Enantioselective effects. Chemosphere 145, 207–214. https://doi.org/10.1016/j.chemosphere.2015.11.035
Wheeler, K.E., Chetwynd, A.J., Fahy, K.M., Hong, B.S., Tochihuitl, J.A., Foster, L.A., Lynch, I., 2021. Environmental dimensions of the protein corona. Nat. Nanotechnol. 16, 617–629. https://doi.org/10.1038/s41565-021-00924-1
White, J.C., Gardea-Torresdey, J., 2018. Achieving food security through the very small. Nat. Nanotechnol. 13, 627–629. https://doi.org/10.1038/s41565-018-0223-y
Wu, H., Li, Z., 2022. Recent advances in nano-enabled agriculture for improving plant performance. Crop J. 10, 1–12. https://doi.org/10.1016/j.cj.2021.06.002
Wu, J., Zhai, Y., Monikh, F.A., Arenas-Lago, D., Grillo, R., Vijver, M.G., Peijnenburg, W.J.G.M., 2021. The differences between the effects of a nanoformulation and a conventional form of atrazine to lettuce: physiological responses, defense mechanisms, and nutrient displacement. J. Agric. Food Chem. 69, 12527–12540. https://doi.org/10.1021/acs.jafc.1c01382
Xiang, Y., Zhang, G., Chi, Y., Cai, D., Wu, Z., 2017. Fabrication of a controllable nanopesticide system with magnetic collectability. Chem. Eng. J. 328, 320–330. https://doi.org/10.1016/j.cej.2017.07.046
Yan, S., Yin, H., Li, N., Chen, Y., Ji, C., Jiang, Q., Du, J., Yin, M., Shen, J., Zhang, J., 2022. Combination of a nanocarrier delivery system with genetic manipulation further improves pesticide efficiency: a case study with chlorfenapyr. Environ. Sci.: Nano 9, 2020–2031. https://doi.org/10.1039/D2EN00126H
Yang, C.-W., Hu, Y., Yuan, L., Zhou, H.-Z., Sheng, G.-P., 2021. Selectively tracking nanoparticles in aquatic plant using core–shell nanoparticle-enhanced raman spectroscopy imaging. ACS Nano 15, 19828–19837. https://doi.org/10.1021/acsnano.1c07306
Yin, R., Gao, L., Qin, D., Chen, L., Niu, N., 2021. Preparation of porous carbon-based molecularly imprinted polymers for separation of triazine herbicides in corn. Microchim. Acta 189, 23. https://doi.org/10.1007/s00604-021-05100-9
Yu, M., Yao, J., Liang, J., Zeng, Z., Cui, B., Zhao, X., Sun, C., Wang, Y., Liu, G., Cui, H., 2017. Development of functionalized abamectin poly(lactic acid) nanoparticles with regulatable adhesion to enhance foliar retention. RSC Adv. 7, 11271–11280. https://doi.org/10.1039/C6RA27345A
Yu, Z., Sun, X., Song, H., Wang, W., ye, Z., Shi, L., Ding, K., 2015. Glutathione-responsive carboxymethyl chitosan nanoparticles for controlled release of herbicides. Mater. Sci. Appl. 06, 591–604. https://doi.org/10.4236/msa.2015.66062
Zainuddin, N.J., Ashari, S.E., Salim, N., Asib, N., Omar, D., Lian, G.E.C., 2019. Optimization and characterization of palm oil-based nanoemulsion loaded with parthenium hysterophorus crude extract for natural herbicide formulation. J. Oleo Sci.
Zeng, X., Zhong, B., Jia, Z., Zhang, Q., Chen, Y., Jia, D., 2019. Halloysite nanotubes as nanocarriers for plant herbicide and its controlled release in biodegradable polymers composite film. Appl. Clay Sci. 171, 20–28. https://doi.org/10.1016/j.clay.2019.01.021
Zhai, Y.J., Monikh, F.A., Wu, J., Grillo, R., Arenas-Lago, D., Darbha, G.K., Vijver, M.G., Peijnenburg, W.J.G.M., 2020. Interaction between a nano-formulation of atrazine and rhizosphere bacterial communities: atrazine degradation and bacterial community alterations. Environ. Sci. -Nano 7, 3372–3384. https://doi.org/10.1039/d0en00638f
Zhang, L., Chen, C., Zhang, G., Liu, B., Wu, Z., Cai, D., 2020. Electrical-driven release and migration of herbicide using a gel-based nanocomposite. J. Agric. Food Chem. 68, 1536–1545. https://doi.org/10.1021/acs.jafc.9b07166
Zhang, P., Guo, Z., Ullah, S., Melagraki, G., Afantitis, A., Lynch, I., 2021. Nanotechnology and artificial intelligence to enable sustainable and precision agriculture. Nat. Plants 7 (864–876), 2021. https://doi.org/10.1038/s41477-021-00946-6
Zhang, X., Xu, Z., Wu, M., Qian, X., Lin, D., Zhang, H., Tang, J., Zeng, T., Yao, W., Filser, J., Li, L., Sharma, V.K., 2019. Potential environmental risks of nanopesticides: application of Cu(OH)2 nanopesticides to soil mitigates the degradation of neonicotinoid thiacloprid. Environ. Int. 129, 42–50. https://doi.org/10.1016/j.envint.2019.05.022
Zhao, L., Huang, Y., Hannah-Bick, C., Fulton, A.N., Keller, A.A., 2016. Application of metabolomics to assess the impact of Cu(OH)2 nanopesticide on the nutritional value of lettuce (Lactuca sativa): enhanced Cu intake and reduced antioxidants. NanoImpact 3–4, 58–66. https://doi.org/10.1016/j.impact.2016.08.005
Zhao, M., Zhou, H., Chen, L., Hao, L., Chen, H., Zhou, X., 2020. Carboxymethyl chitosan grafted trisiloxane surfactant nanoparticles with pH sensitivity for sustained release of pesticide. Carbohydr. Polym. 243, 116433. https://doi.org/10.1016/j.carbpol.2020.116433
Zhao, X., Cui, H., Wang, Y., Sun, C., Cui, B., Zeng, Z., 2018. Development strategies and prospects of nano-based smart pesticide formulation. J. Agric. Food Chem. 66, 6504–6512. https://doi.org/10.1021/acs.jafc.7b02004
Zhong, B., Wang, S., Dong, H., Luo, Y., Jia, Z., Zhou, X., Chen, M., Xie, D., Jia, D., 2017. Halloysite tubes as nanocontainers for herbicide and its controlled release in biodegradable poly(vinyl alcohol)/starch film. J. Agric. Food Chem. 65, 10445–10451. https://doi.org/10.1021/acs.jafc.7b04220
Ziv, C., Zhao, Z., Gao, Y.G., Xia, Y., 2018. Multifunctional roles of plant cuticle during plant-pathogen interactions. Front. Plant Sci. 9.